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DETERMINATION OF SULPHUR IN ILLUMINATING GAS

BY

R. S. McBRIDE, Assistant Chemist
and
E. R. WEAVER, Laboratory Assistant
Bureau of Standards

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By R. S. McBride and E. R. Weaver

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I. APPARATUS AND METHODS EMPLOYED

The methods for determination of sulphur in gaseous fuels can be classified into four groups, the general principles of which are as follows:

1. The gas is burned and the sulphur oxides in the products of combustion are condensed or absorbed, oxidized to sulphate, and determined as such.

2. The sulphur compounds are oxidized by liquid reagents giving the sulphate, which can be determined directly.

3. The sulphur compounds are oxidized by burning the gas, but the sulphur is absorbed and determined as sulphur dioxide.

4. The sulphur compounds are reduced to give hydrogen sulphide, which is then absorbed and determined.

The methods of group 1 have been most used in American practice and are generally considered the most accurate and convenient, either for works control or official testing. Five distinct forms of apparatus of this general class and some variations of them have been tried, and the report of these tests is given in detail in the following sections. In these investigations the relative accuracy and convenience of the various forms were considered with the idea of determining the best conditions for operation of each. In describing our experience with these apparatus some of the points are discussed in detail in order to assist inexperienced operators to a rather full understanding of the reasons for some precautions and directions given.

The methods of groups 2 and 4 are probably least used, and they are also perhaps subject to the greatest inaccuracies, since in either the wet oxidation or the reduction to hydrogen sulphide it seems certain that not all of the sulphur in various kinds of gas is completely oxidized or reduced, so that the results are too low. The few tests made on these methods gave very unsatisfactory results. In the case of the method of reducing to hydrogen sulphide the deposition of large amounts of carbon on the catalyzer was a constant source of difficulty.

The methods of group 3, particularly the method of Somerville, have been used to some extent, and it appears probable that a modification of the Somerville method could be used, if desired, for rapid and approximate determination in works control. Brief attention is given to such a method on page 12.

1. REFEREES APPARATUS

The apparatus most often used in this country for official or works control determination of total sulphur is that of the Metropolitan Gas Referees, specified for official use in London. This

apparatus is described as follows in the Notification of the Gas Referees for the Year 1913:

The gas is burnt in a small Bunsen burner with a steatite top, which is mounted on a short cylindrical stand perforated with holes for the admission of air and having on its upper surface, which is also perforated, a deep circular channel to receive the wide end of a glass trumpet tube. There are both in the side and in the top of this stand 14 holes of 5 millimeters in diameter, or an equivalent airway. On the top of the stand, between the narrow stem of the burner and the surrounding glass trumpet tube, are to be placed pieces of commercial sesquicarbonate of ammonia, weighing in all about 2 ounces.

The products both of the combustion of the gas and of the gradual volatilization of the ammonia salt go upward through the trumpet tube into a vertical glass cylinder with a tubulure near the bottom, and drawn in at a point above this to about half its diameter. From the contracted part to the top the cylinder is packed with balls of glass about 15 millimeters in diameter to break up the current and promote condensation. From the top of this condenser there proceeds a long glass pipe or chimney tube slightly bent over at the upper end, serving to effect some further condensation, as well as to regulate the draft and afford an exit for the uncondensable gases. * * * In the bottom of the condenser is fixed a small glass tube, through which the liquid formed during the testing drops into a flask placed beneath. * * * The lower end of this tube is contracted so that when in use it may be closed by a drop of water.

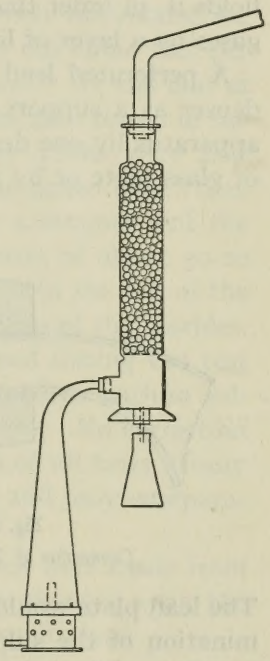

Fig. 1.—*Referees Apparatus*

In the apparatus first used by us the top of the trumpet tube was introduced into the tubulure of the condenser, a tight joint being made by a thin rubber stopper. But our experience showed that a rubber connection of any kind at this point is undesirable, since the upper end of the trumpet tube becomes very hot and sulphur may be introduced into the apparatus from the rubber. The first time a new rubber connection was used on such an apparatus it caused an error of 60 per cent in the sulphur found A ground-glass connection at this point would be the best except for its fragility; but a soft, well-fitting cork was found to make a tight connection when used in either of two ways. If the tubulure and trumpet tube are about the same size, Fig. 2*a* shows the simplest method of connection; if the trumpet tube is consider-

ably smaller than the tubulure, as is the case with the apparatus sold by some makers, connection can be made as in Fig. 2*b*.

As has been already stated, the use of a rubber connector as illustrated in the "Notification" of the London referees, or substitution of rubber for cork in the form of Fig. 2*b* is not desirable.

It is best to allow the small glass outlet tube at the base of the condenser to project slightly above the rubber stopper which holds it, in order that the stopper may be protected from the hot gases by a layer of liquid.

A perforated lead plate, to be used at the bottom of the condenser as a support for the glass marbles, is furnished with the apparatus by one dealer. This should be replaced by a porcelain or glass plate or by a support made of glass rod bent to S shape.

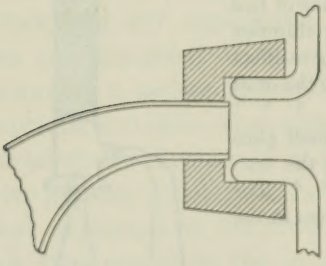

Fig. 2a

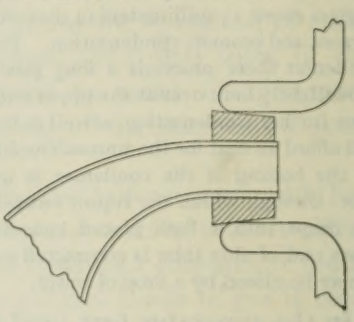

Fig. 2b

Connection of Trumpet Tube and Condenser in Referees Apparatus

The lead plate would always be likely to cause errors in the determination of the sulphate, and would certainly do so during the first few runs while a film of lead sulphate was forming over the metal surface. When setting up the apparatus, it is best to fill the condenser cylinder with water, so that the marbles may be dropped in without danger of breaking it.

Two condensers of different shapes, representing the forms furnished by two different dealers in apparatus, were used at this Bureau, the space occupied by marbles in one having an internal diameter of 6 cm and a height of 30 cm, in the other of 7 and 18 cm, respectively. Although differing by about 25 per cent in size, the two gave practically the same efficiency of condensation, judging by the values obtained. (See comparison of

Table 1.) At the beginning of the tests made with them the two models were run practically as specified in the 1912 "Notification," above refereed to. Large pieces of ammonium carbonate, freed from efflorescent portions, were placed about the burner stem and the gas was lighted. After burning long enough to purge the meter and connections, the trumpet tube was slipped over the burner and connected with the condenser quickly, the meter reading being noted at the instant when the connection was made; and the gas was burned at 0.4 to 0.6 cubic feet per hour for the desired period (from 2 to 8 hours). At the end of this time the apparatus was allowed to cool and then rinsed in the following manner: The trumpet and chimney tubes were first disconnected from the condenser and each was rinsed once; then the tubulure of the condenser was closed by a stopper and the marbles were rinsed with three portions of water of about 50 cc each, the portions of wash water being poured into the top of the condenser quickly in order to flush all the surfaces of the marbles. All washings and the condensed liquid obtained during the test were combined and the sulphate was determined as barium sulphate by the method described in a later section. No correction for pressure or temperature was necessary, since all tests at any one time were run under the same conditions and only comparative values were needed.

Variations from this general procedure, which were made from time to time to investigate the effect of these changes upon the results, will be indicated in the report of the results later.

2. ELLIOTT APPARATUS

The original form of Elliott apparatus, illustrated in Fig. 3, has been used to some extent; but in most cases it is being replaced, as it has been found too fragile for ordinary use. In referring to the later form of apparatus, which is illustrated in Fig. 4, Dr. Elliott[1] says: "This is the latest modification of sulphur apparatus and is the one we prefer to use, because it is less fragile than the ones formerly used, which were readily broken." Because of the infrequency of its use only a few tests were made upon the older form of apparatus.

[1] Private communication to this Bureau.

The new form devised by Dr. A. H. Elliott has not been fully described by him in any publication, only a brief reference to it being found in Baskerville's Municipal Chemistry (p. 319). Fig. 4 shows the form preferred by the originator, as given to the Bureau in a private communication. The porcelain Bunsen burner, with a perforated porcelain plate near the top, supports pieces of ammonium carbonate. A trumpet tube resting on the plate conveys the products of combustion mixed with ammonia to the top of the first condenser (a 24-inch calcium chloride tower). The tubulure at the bottom of this cylinder is connected with that of the second cylinder of the same kind. Glass tubes drawn down to small tips are fitted into rubber stoppers in the bottom of each tower, allowing the condensate to drip into flasks placed beneath.

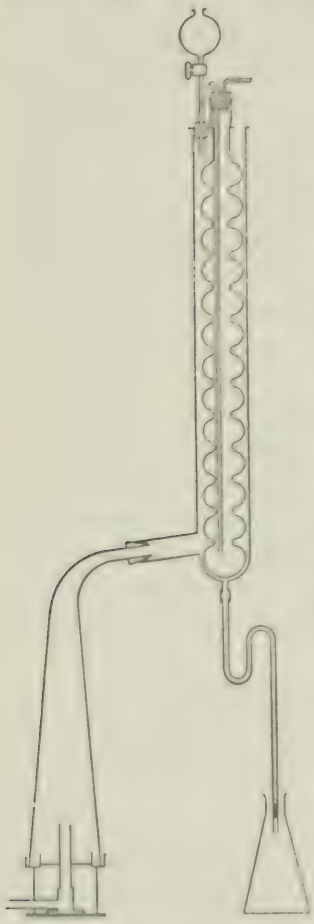

Fig. 3.—*Old Model Elliott Apparatus*

The apparatus as designed by Dr. Elliott had a rubber adapter at the top of the short trumpet tube, connecting it with the bent tube leading to the first condenser. This rubber connection should be removed and the two tubes sealed together to prevent sulphur being introduced from the rubber. A well-fitting cork stopper serves to connect the trumpet tube to the condenser, and as the gases are well cooled before reaching the bottom of the tower the use of a rubber connection at that place is permissible. As can be seen from the figure, the principle and general form of the apparatus is similar to that of the Referees.

The new-form Elliott apparatus was operated in the same general manner as the Referees, the principal changes being in rate

of burning of the gas and amount of water required for washing. The gas was burned usually at from 0.7 to 1 cubic foot per hour.

The older form of Elliott apparatus (Fig. 3 above) requires the use of water to cool the bulb condenser. Two methods of introducing the alkali for absorbing the sulphur oxides are available: First, use of ammonium hydroxide or ammonium carbonate at

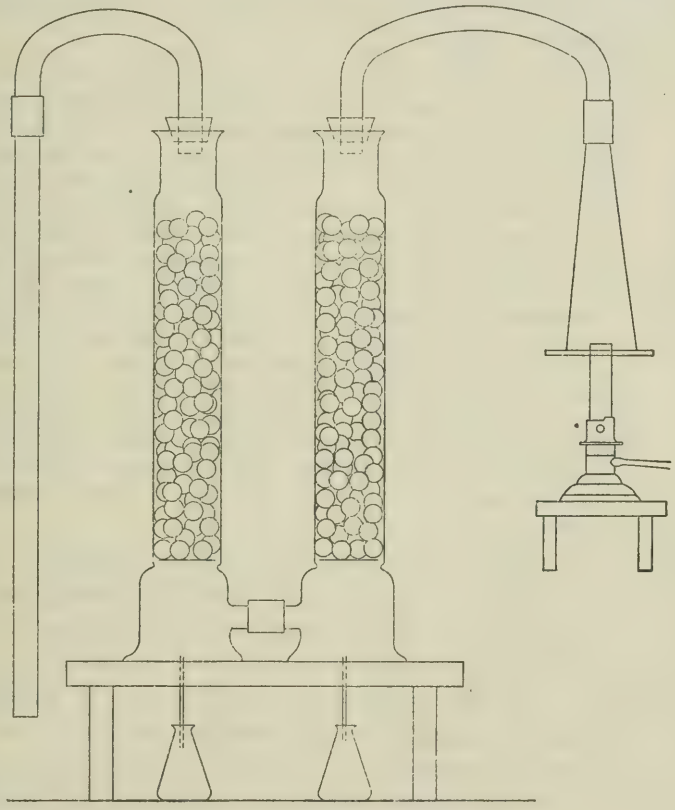

Fig. 4.—*New Model Elliott Apparatus*

the burner, as in the Referees or Hinman-Jenkins apparatus; and, second, use of alkaline solutions run in at the top of the condenser. For the first comparisons made (see Table 2) sodium hydroxide was run in at the top of the condenser; but the presence of volatile alkali was found necessary, and for the later tests ammonium carbonate about the burner was found most convenient. The gas

was burned at the rate of 0.4 to 0.6 foot per hour and the washing of the condenser accomplished with about 200 to 300 cc of water, as in the case of the Referees apparatus.

3. HINMAN-JENKINS APPARATUS

The apparatus, known by the names of its inventors as the Hinman-Jenkins form, is illustrated in Fig. 5. It is described by Jenkins[2] in the following words:

> The upper vessel is a "bead glass" 300 mm long and 60 mm in diameter; this is filled with large cut glass beads, held up by a suitable fluted glass, giving a large condensing surface without obstructing the draft. To this bead glass is attached, by a rubber connector, the adapter, 410 mm long and 50 mm lower internal diameter. To the upper adapter is attached, by means of the "connecting piece," the lower adapter, 400 mm long and 40 mm lower diameter. The connecting piece projects 12 mm above the top of a rubber stopper, fitting the upper adapter, and is surmounted by a watch-glass deflector carried on platinum wires. An overflow tube carries the condensation to the Erlenmeyer flask hung on the stopper as shown; this tube is so adjusted that some liquid remains on the stopper to keep it cool and to absorb some of the ascending gases. The Bunsen burner is fitted with a lava tip having a 5-mm hole; surrounding the burner is a glass tube 20 mm in diameter, forming the inner wall of an annular chamber, of which the outer wall is a glass ring 50 mm in diameter. Into this chamber, which serves to contain 10 per cent ammonium hydroxide, the lower adapter dips 10 mm.

Fig. 5.—*Hinman-Jenkins Apparatus*

The lower adapter is joined to the "connecting piece" by a short cork-lined metal tube. Although radically different in form, this apparatus is very similar to the Referees in general principle and in method of use, the principal difference being the use of ammonium hydroxide instead of dry ammonium carbonate as a source of ammonia. About 10 cc of concentrated ammonium hydroxide is placed in the reservoir about the burner at the beginning of the test and about 5 cc more added every 15 or 20 minutes. The gas was burned at the rate of 0.4 to 0.6 cubic foot per hour. When the run was completed the apparatus was allowed to cool and was then flushed four times by pouring 50 cc portions of water in at the top of the bead tube.

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[2] Jour. Am. Chem. Soc., 28, pp. 543–545; 1906.

4. DREHSCHMIDT APPARATUS

The original form of the Drehschmidt [3] apparatus, shown in Fig. 6, is used in a few laboratories in this country.

In this apparatus the gas is burned in a metal Bunsen burner under the chimney tube, which rests in a mercury seal, so that all air passing through the apparatus must enter through the air tubes at the base of the burner chamber. This air is drawn in through a tower containing marbles wet with alkali, which prevent entrance of sulphur compounds with the air. The products of

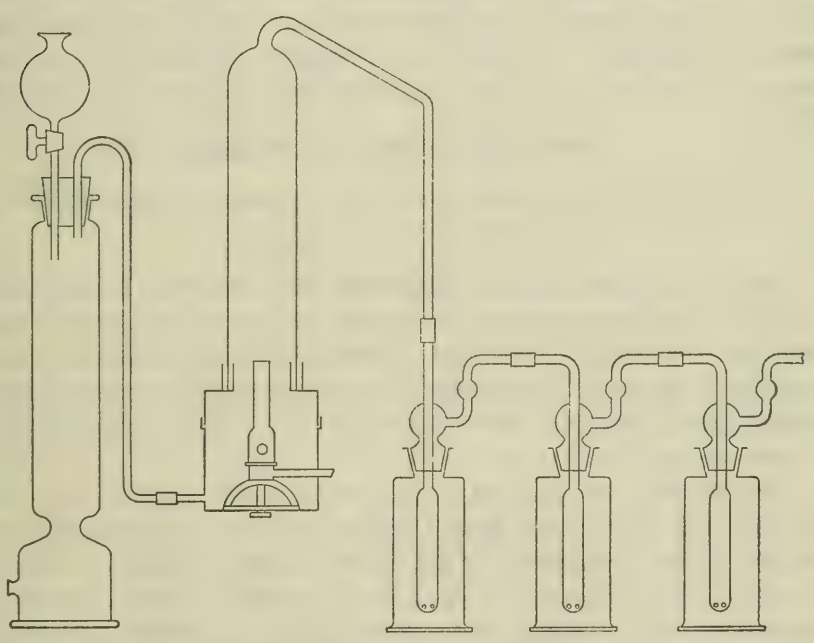

Fig. 6.—*Drehschmidt Apparatus*

combustion are drawn out through the three gas washing bottles, which contain potassium carbonate solution and bromine to condense and oxidize the sulphur oxides.

The gas was burned in this apparatus at about 1 cubic foot per hour and the products of combustion were drawn through the three wash bottles as indicated above. The general procedure described by the originator of this process was followed closely in the use of the apparatus for the few tests made with it.

[3] Chem. Ztg., **11**, p. 1382; 1887.

5. MODIFIED DREHSCHMIDT APPARATUS

The majority of the modifications of this apparatus are made almost wholly of glass and are intended for very exact work rather than for works control or official testing. One of these, which can be put together from simple apparatus to be had in any chemical laboratory, is that described by Harding.[4] The greatest difficulty met in the use of this latter is that of keeping the burner lighted, as slight fluctuations of air or gas pressure cause it to go out. To overcome this difficulty a modification of the burner was made and used in an apparatus of somewhat more convenient form than that used by Harding. This burner, in the form recommended for use where an apparatus of this general group is desired, is shown in Fig. 7.

6. MODIFIED SOMERVILLE APPARATUS

The method described by Somerville [5] is based on the reaction:

$$SO_2 + 2I + 2H_2O = H_2SO_4 + 2HI$$

The apparatus consists essentially of a Bunsen burner surrounded by a trumpet tube from which the products of combustion are drawn through a gas wash bottle containing standard iodine solution. Because the original apparatus seemed unnecessarily complicated, fragile, and expensive the simple modification shown in Fig. 8 was used.

For the first tests 5 g of tenth normal iodine solution was run into the gas wash bottle from a weight burette and diluted to 300 to 400 cc; and the amount of gas burned before the solution became decolorized was noted. Since it was found that a large error was caused by loss of iodine through volatilization, more iodine was used and a second wash bottle containing a known amount (about 3 g) of tenth normal sodium thiosulphate diluted to 200 cc was added. Before the iodine solution was entirely decolorized the two solutions were mixed and titrated with one or the other standard solution, depending upon which was in excess, using starch as an indicator. From the difference between the amount of iodine and thiosulphate used the sulphur contained in the gas was calculated.

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[4] Jour. Am. Chem. Soc., **28**, p. 517; 1906.

[5] Jour. Gas Lighting, **112**, p. 28; 1910.

II. EXPERIMENTAL PART

To compare the several forms of apparatus, two or more were operated at the same time, being supplied by gas from a common source. The connections from gas supply to meters and from

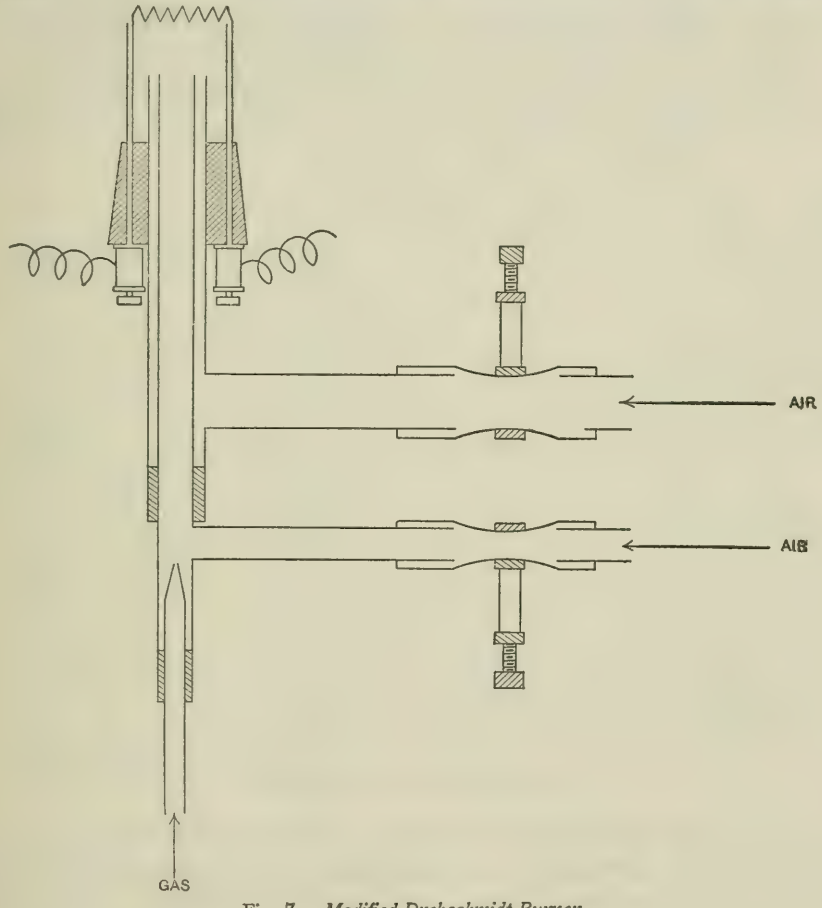

Fig. 7.—*Modified Drehschmidt Burner.*

meters to apparatus were largely of glass, in order that no sulphur should be introduced into or removed from the gas supplied by the rubber tubing and that the possibility of leakage through the tubing would be minimized. To purge each line so that gas of the same character was supplied for each burner, the gas was

burned for a short time before each comparison was begun. It was considered improbable that the difference in rate of passage of the gas through the different meters would cause an appreciable difference in the amount of sulphur compounds which might be taken up by the liquid in the meters; and this is probably the only way in which a difference in the character of gas supplied to the different burners could have been brought about.

The meters employed were filled with 5 per cent glycerin to make changes in water level less rapid. They were run in series

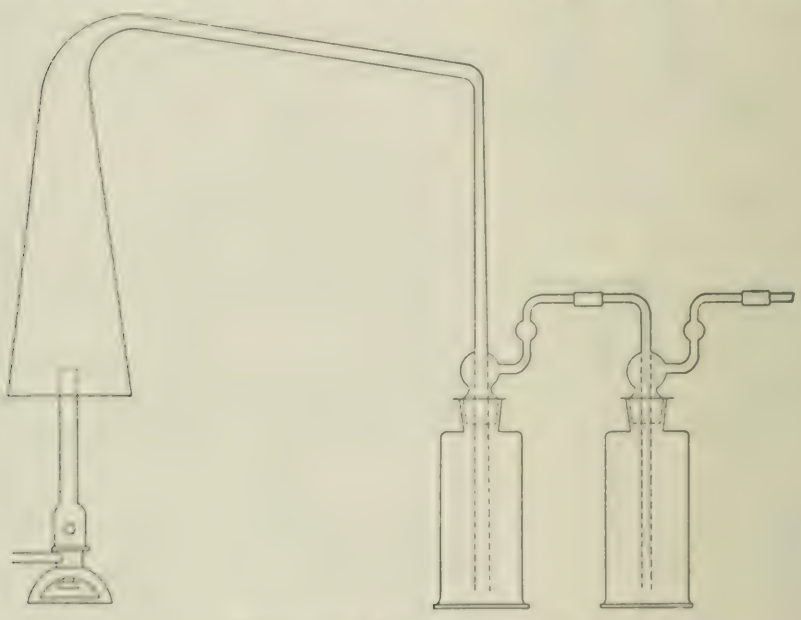

Fig. 8.—*Modified Somerville Apparatus.*

to determine their relative accuracy, in all cases the results showing very fair agreement; and the small corrections indicated by the tests were made upon the observed readings. Frequent recomparison of meters after continued use showed almost exact agreement with the values obtained before use. Very little change in water level was noted over long periods, since the 5 per cent glycerin was taken up by the gas very much more slowly than would have been the case with water. However, for use in ordinary work it is not recommended that meters be filled

with any other liquid than water because of the uncertain solvent action of various solutions upon the gas. For our work, where only relative values were needed, this factor was not of importance.

It was proved that at various rates less than 5 cubic feet per hour the gas became practically equally charged with water on the passage through the meters, so that in cases where two apparatus were run at different rates the gas measurement was not appreciably affected by differences in saturation.

1. APPARATUS WITH AIR-COOLED CONDENSERS

(*a*) GENERAL COMPARISONS

A series of comparisons of the Referees, new Elliott, and Hinman-Jenkins apparatus, in which many variations were made to determine the best conditions of operation, the sources of error, etc., is partly summarized in Tables 1 and 2. The results tabulated, however, include only those obtained under normal working conditions and not those obtained when variations were made which would be avoided in practice. The tables give a fair idea of the variations which may be expected in practical operation, as all results thus obtained are included.

Except as otherwise noted, the sulphate in the condensed liquids was determined as barium sulphate by the first method given in Part IV of this paper (p. 33); and except in tests reported in Table 2 no corrections were made for silica. Other gas flames were allowed to burn in the room only when necessary. The error from this latter source is small, because the amount of air taken in by each apparatus was roughly proportional to the amount of gas burned.

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TABLE 1

Preliminary Comparison of the Referees, Elliott, and Hinman-Jenkins Apparatus

THE GAS BURNED IN THE ELLIOTT APPARATUS AT 0.96 CUBIC FOOT PER HOUR, AND IN THE OTHER THREE AT 0.60 CUBIC FOOT PER HOUR.

Test	Referees No. 1 (sulphur per 100 cubic feet of gas)	Referees No. 2 (sulphur per 100 cubic feet of gas)	Ratio Referees No. 2 to Referees No. 1	Elliott (sulphur per 100 cubic feet of gas)	Ratio Elliott to Referees No. 1	Hinman-Jenkins (sulphur per 100 cubic feet of gas)	Ratio Hinman-Jenkins to Referees No. 1	Ratio Elliott to Hinman-Jenkins
	Grains	*Grains*	*Per cent*	*Grains*	*Per cent*	*Grains*	*Per cent*	*Per cent*
1	13.7	.....	.....	13.2	97.3	14.0	102.7	94.5
2	12.8	12.3	96.6	14.3	110.7	13.6	106.3	105.0
3	13.0	13.0	100.0	.....	.....	14.2	108.9	.....
4	13.9	14.6	104.8	.....	.....	13.2	94.5	.....
5	12.9	12.3	95.2	.....	.....	14.2	111.9	.....
6	12.4	13.6	109.7	13.2	106.7	14.0	113.2	94.5
7	13.6	13.8	101.7	13.7	101.4	14.4	107.7	95.2
8	13.8	13.4	97.2	14.2	103.0	15.0	108.8	94.6
9	15.0	.....	.....	15.2	100.8	15.9	106.1	95.5
Average ratio	.....	.....	100.7	.....	104.5	.....	106.7	96.5

In the series given in Table 2 all determinations were made in a room free from other flames, and the results were corrected for silica. The results of experiments 18 to 23 show clearly the effect of changing the rate of gas consumption.

TABLE 2

Final Comparison, with Gas Burning at Specified Rates, of the Referees, Elliott, and Hinman-Jenkins Apparatus

REFEREES 0.60, ELLIOTT 0.96, HINMAN-JENKINS 0.60 CUBIC FOOT PER HOUR

Test	Referees No. 1 (sulphur per 100 cubic feet of gas)	Referees No. 2 (sulphur per 100 cubic feet of gas)	Ratio Referees No. 2 to Referees No. 1	Elliott (sulphur per 100 cubic feet of gas)	Ratio Elliott to Referees No. 1	Hinman-Jenkins (sulphur per 100 cubic feet of gas)	Ratio Hinman-Jenkins to Referees No. 1	Ratio Elliott to Hinman-Jenkins
	Grains	*Grains*	*Per cent*	*Grains*	*Per cent*	*Grains*	*Per cent*	*Per cent*
10	11.3	11.5	101.9	10.9	98.2	.....	.....	.....
11	13.8	13.5	97.8	14.3	103.6	13.8	100.0	103.7
12	13.9	13.9	100.0	14.8	106.6	14.7	106.0	100.8
13	13.4	.....	.....	13.9	104.1	13.7	103.3	101.3
14	13.4	.....	.....	12.6	93.8	14.0	104.7	90.0
15	13.5	.....	.....	14.8	109.9	14.0	103.7	106.0
16	13.8	.....	.....	.....	.....	14.0	101.0	.....
17	13.6	.....	.....	.....	.....	13.8	101.5	.....
Average ratio	.....	.....	99.9	.....	102.7	.....	102.9	100.3

REFEREES 0.49, ELLIOTT 1.20, HINMAN-JENKINS 0.65 CUBIC FOOT PER HOUR

18	15.2	.....	.....	14.9	98.0	14.3	94.0	104.1
19	13.9	.....	.....	14.0	101.0	13.0	93.6	107.8
20	14.3	.....	.....	.....	.....	13.3	93.0	.....
21	15.4	.....	.....	.....	.....	14.4	93.5	.....
22	13.1	.....	.....	13.1	100.0	12.9	98.5	101.7
23	13.2	.....	.....	.....	.....	12.2	92.5	.....
Average ratio	.....	.....	.....	.....	99.7	.....	94.2	104.4

REFEREES 0.50, ELLIOTT 1.20, HINMAN-JENKINS 0.50 CUBIC FOOT PER HOUR

24	13.8	.....	.....	15.0	108.5	13.9	100.7	107.9
25	10.3	.....	.....	9.9	96.0	9.9	96.0	100.0
26	16.1	.....	.....	16.6	103.0	.....	.....	.....
27	13.5	.....	.....	.....	.....	13.9	102.6	.....
28	11.6	.....	.....	.....	.....	12.1	103.9	.....
29	13.2	.....	.....	.....	.....	13.0	98.3	.....
Average ratio	.....	.....	.....	.....	102.5	.....	100.3	103.9

These data of Tables 1 and 2 showed that the two models of Referees apparatus agreed with each other very well, and therefore that the difference in size of these two condensers has no appreciable effect upon the experimental results. On the other hand, the Hinman-Jenkins and the Elliott apparatus, while agreeing with each other, almost always give results somewhat higher than those obtained with the Referees apparatus. These differences could be ascribed only to a difference in the efficiency of the condensation of the sulphur oxides, and the exact cause of this difference was the next point considered.

(b) EFFICIENCY OF CONDENSATION

Three important factors affecting the efficiency of condensation of the sulphur in the products of combustion were considered, viz, the amount of condenser surface, the rate of burning of the gas, and the alkalinity of the atmosphere in the condenser chamber.

Size of Condenser.—The two makes of Referees apparatus used differed in size mainly in the condenser chamber, which was 25 per cent larger in the one than in the other case. As shown in Tables 1 and 2, these two models give results in very good agreement with each other. It is, therefore, certain that differences in size of condensers such as were used in this case have little effect upon the results.

As no cause was apparent for the lower results obtained with the Referees than with the other apparatus, except possible losses of sulphur with the products of combustion, tests were made upon the escaping gases to detect if possible sulphur dioxide or sulphur trioxide. The products were passed over the surface of a solution of barium chloride, hydrochloric acid, and bromine, but no precipitate of barium sulphate could be detected after passing all the products of burning for three hours over such solution. Although no sulphur could be found in the products by this method, it was decided to increase the condenser capacity of the Referees apparatus by adding a second bead tower at the top of the first; this practically doubled the size of the condenser. The condensed liquid from the two towers was collected and the sulphur determined independently in order to determine the amount of sulphur which ordinarily escaped from the single

tower. The results of these tests, as given in Table 6, show that about 1 to 3 per cent of all the sulphur was condensed in the extra tower, and it is probable that about this amount of sulphur escaped uncondensed from the apparatus as regularly operated. This loss, therefore, accounts for the lower results obtained with this apparatus, and it indicates the necessity of a larger condenser or modified method of operation for the Referees form of apparatus if great accuracy of test is required.

The Elliott apparatus, which has much more condensing surface than the Referees could be safely operated at higher rates of gas consumption. This point will be discussed in the next section.

Amount of Gas Burned.—The effect of varying the rate at which the gas was burned, shown in Table 2, is still better indicated in Table 3, which shows the percentage of sulphur condensed in each tower of the Elliott apparatus with the gas burning at three different rates. In every case the sulphur condensed in the trumpet tube is combined with that collected in the first tower. The significance of the results appears at once when we remember that the first tower with its connections is practically a large Referees apparatus and the sulphur which passes into the second tower is practically all lost in the Referees form.

It appears that there is a certain rate of combustion for each apparatus beyond which the loss of sulphur becomes serious. From our experiments we believe that if the ammonium carbonate or hydroxide is renewed as frequently as recommended later, 1.0 cubic foot per hour for the Elliott and 0.5 cubic foot for the other forms of apparatus are safe rates. The losses increase rapidly at higher rates.

TABLE 3

Amount of Sulphur Condensed in Different Parts of the Elliott Apparatus at Different Rates of Gas Consumption

Rate (cubic feet per hour)	Sulphur in first tower (grains per 100 cubic feet of gas)	Sulphur in second tower (grains per 100 cubic feet of gas)	Total sulphur (grains per 100 cubic feet of gas)	Per cent of total condensed in second tower	Referees burned at 0.5 cubic foot per hour (sulphur, grains per 100 cubic feet of gas)
1.36	5.7	3.7	9.4	39	15.5
	8.2	4.7	12.9	36	14.2
	4.9	1.5	6.4	23	11.5
1.20	13.9	1.1	15.0	8	13.8
	9.4	0.5	9.9	6	10.3
	14.8	1.8	16.6	8	16.1
0.9	11.5	1.7	13.2	8	13.7
	10.4	3.9	14.3	3	12.8
	10.7	2.5	13.2	2	12.4
	12.1	1.6	13.7	1	13.6
	12.2	2.0	14.2	8	13.8
	13.1	2.1	15.2	1	15.0

Indeed the amount of sulphur condensed per hour in the Elliott apparatus was less when the gas was burning at the rate of 1.36 cubic feet than when burning at 1.20 cubic feet per hour.

Alkalinity of Air in Condenser Chamber.—Our work throughout indicated that the most serious source of error in any apparatus of this type is an insufficient or irregular ammonia supply.

Table 4 shows the effect of using in the Referees apparatus lumps of carbonate which had previously been used and which were, therefore, deeply incrusted with bicarbonate. As much ammonium carbonate was used in each case as would lie in the annular space about the burner. From the decrease in efficiency of condensation on long use of the carbonate, shown by the results of Table 4, it appears that a 10-hour run, using a single supply of carbonate, could hardly be expected to give more than 90 to 95 per cent or a 20-hour run more than 75 to 80 per cent of the sulphur burned.

TABLE 4

Effect of Using Old Ammonium Carbonate on Referees Apparatus

Test	Previous use of carbonate	Length of run	Sulphur condensed with old carbonate (A)	Sulphur condensed with fresh carbonate (B)	Ratio of (A) to (B)
	Hours	*Hours*	*Grains*	*Grains*	*Per cent*
30	6	6.5	7.0	14.0	50
31	6	6.5	11.5	14.9	77
32	6.5	6	9.5	13.9	78
33	6	6	11.0	13.6	81
34	([6])	([6])	5.1	16.8	30

[6] No carbonate used.

Table 5 shows the effect of varying the ammonia supply to the Elliott apparatus upon the percentage of the total sulphur which escapes from the first tower and is collected in the second. Similarly, Table 6 shows the percentage of total sulphur collected in the added condenser of the Referees apparatus previously mentioned (p. 18), first, when nothing was added to this second condenser; second, when concentrated ammonium hydroxide was slowly dropped in at the top of the second condenser; and third, when a solution of hydrogen peroxide and ammonium hydroxide was added in the same way. The object of adding hydrogen peroxide was to see what effect an oxidizing substance would have upon the absorption of the sulphur dioxide; but from the results obtained this effect appears to be negligible. In each case the apparatus was run in the same manner as in previous determinations, burning gas at the rate of 0.49 cubic feet per hour, the only change being in the added condenser. With this added condenser the performance of the apparatus was equal to the best results obtained from the Elliott apparatus.

TABLE 5

Percentage of Total Sulphur Condensed in Second Tower of Elliott Apparatus Burning 1.2 Cubic Feet of Gas per Hour

$(NH_4)_2CO_3$ renewed every 3 hours	$(NH_4)_2CO_3$ renewed every hour	Air supplied to apparatus bubbled through concentrated NH_4OH
Per cent	*Per cent*	*Per cent*
7.5	0.6	0.1
6.0	0.8	.....
8.0	.....	.....

TABLE 6

Percentage of Total Sulphur Condensed in Added Condenser of Referees Apparatus

Nothing added to second condenser	NH_4OH added to second condenser	$NH_4OH + H_2O_2$ added to second condenser
1.0	3.6	1.2
1.1	2.2	2.3
.8	0.9	2.0
.....	.....	1.0
Average, 1.0	2.2	1.6

In this connection it may be well to call attention to the higher results shown in Table 8 obtained with the old-form Elliott apparatus when using ammonium carbonate around the burner, than when running in sodium carbonate at the top of the condenser. The difference is due to an alkaline atmosphere as compared with a condensing surface covered with an alkaline liquid.

(*c*) AMOUNT OF WASH WATER REQUIRED

The Referees' "Notification" for 1912 states: "The condenser is then to be flushed twice or thrice by pouring quickly into the mouth of it 40 or 50 cubic centimeters of distilled water." However, results of our tests reported in Table 7 indicate that the use of at least four portions of wash water is desirable.

In a large number of tests it was found that the chimney tube of the Elliott and Referees forms did not contain appreciable amounts of condensed sulphur; nor does the ammonium hydroxide vessel about the Hinman-Jenkins burner take up any sulphur. However, in all forms of apparatus the trumpet tube which forms the burner chamber must be rinsed out, since from 0.5 to 1.0 mg of sulphur condenses as sulphate on the walls of this portion of the apparatus.

TABLE 7

Number of Washings Required to Collect Condensate

Washings [7]	Percentage of total sulphur collected		
	Elliott	Hinman-Jenkins	Referees
2	95.7	97.4	96.2
3	98.1	99.0	98.2
4	99.5	99.8	99.2
5	100	100	100

[7] For the Elliott 100 cc portions of wash water were used, but for the other two forms 50 cc portions were employed. The total obtained by five washings is taken as 100 per cent.

2. APPARATUS WITH WATER-COOLED OR LIQUID CONDENSATION

The early form of Elliott apparatus used a water-cooled condenser (as shown in Fig. 3), and the Drehschmidt apparatus and all modifications of it condense the sulphur by bubbling the products of combustion through liquids. These two types of apparatus, especially the latter, differ so greatly in principle from the Referees and other forms which have air-cooled condensers that they can be best considered separately.

Table 8 gives a series of comparisons between the Referees and the two forms of Elliott apparatus.

TABLE 8

Comparison of the Referees and Two Models of Elliott Apparatus

Test	Referees (sulphur per 100 cubic feet)	Old-form Elliott		New-form Elliott	
		Sulphur per 100 cubic feet	Ratio to Referees	Sulphur per 100 cubic feet	Ratio to Referees
	Grains	*Grains*	*Per cent*	*Grains*	*Per cent*
6	7.3	2.9	40		
7	8.4	3.9	46	9.2	109
8	8.4	3.3	40	9.8	116
9	8.2	2.5	30	8.5	104
10	7.9	8.4	106	7.8	99
11	7.9	8.3	105	8.2	104
12	8.0	8.0	100	8.3	104
13	8.4	8.1	97	8.7	104
14	15.5	15.8	102	15.9	103
15	13.9	14.5	104	14.8	106
16	13.7	12.2	90	13.2	96

For the first four comparisons the old form of Elliott was operated without ammonium carbonate or ammonium hydroxide, only sodium hydroxide being introduced at the top and allowed to run down over the condenser bulbs, but in the other seven comparisons ammonium carbonate crystals were used as with the Referees.

Although when using ammonium carbonate with the old-form Elliott results of satisfactory accuracy can be obtained, yet the fragility and inconvenience of form do not make it a desirable apparatus for general use. As has been above indicated, its originator has been led to use the later model because of its greater convenience and strength.

The comparisons reported in Table 9 were made with the Referees and the original Drehschmidt. Only a few results were obtained, since the burner adjustment could be made with difficulty with the Drehschmidt apparatus, and on numerous trials the mixtures of gas and air in the burner chamber exploded or the flame was extinguished by lack of air. The apparatus was finally abandoned as being too inconvenient for general use.

The principle of condensation of the sulphur by bubbling the products of combustion through an alkaline liquid seems very

good, but for practical purposes the air-cooled condensers of the type of the Referees apparatus are sufficiently satisfactory; the latter type also does not require the use of suction. When used in a room where other gas is burning the apparatus of the Drehschmidt type has the advantage that the air entering does not carry in sulphur, but if the apparatus is properly used this factor is not serious.

TABLE 9

Comparison of the Referees and Drehschmidt Apparatus

Test	Referees (sulphur per 100 cubic feet)	Drehschmidt (sulphur per 100 cubic feet)	Ratio Drehschmidt to Referees
	Grains	*Grains*	*Per cent*
1	16.1	17.2	107
2	16.6	16.8	101
3	15.7	15.5	99
4	15.9	13.4	84
5	15.5	12.9	83

The comparisons made between the Referees and the modified Somerville apparatus are reported in Table 10. No extended tests were made to determine the exact operating conditions which would be best to use, since this procedure is little used and is not particularly well adapted for works use, or official testing.

TABLE 10

Comparison of the Referees and Modified Somerville Apparatus

Referees (sulphur per 100 cubic feet)	Modified Somerville (sulphur per 100 cubic feet)	Ratio Somerville to Referees
Grains	*Grains*	*Per cent*
15.2	13.7	91
15.2	15.2	100
14.3	12.4	87
16.4	17.4	106
15.4	15.9	103
16.8	15.5	92
14.3	14.4	101
15.7	14.9	95
15.5	15.1	97

III. RECOMMENDATIONS AS TO FORM AND OPERATION OF APPARATUS

1. MERITS OF VARIOUS APPARATUS

As has already been said, the methods in which the sulphur compounds are reduced to hydrogen sulphide and those in which oxidation of the sulphur is accomplished by a liquid are not sufficiently accurate except possibly for works control. They seem to have no particular advantages even in speed, since the Somerville method when properly carried out is the most rapid of all and considerably more accurate than the two groups just mentioned. However, use of the Somerville apparatus requires considerable skill and chemical knowledge, and the method is not as generally practicable as other methods.

Only the apparatus of the Referees or the Drehschmidt type seem reasonably satisfactory for general use in official testing of gas, but there is some difference of opinion as to the relative merits of the apparatus of these two groups. The apparatus with air-cooled condensers (Referees, Hinman-Jenkins, and Elliott) are most often used, being simpler, less fragile, and more convenient for frequent use; but the forms of apparatus in which the sulphur is condensed by a liquid reagent seem to give greater surety of complete condensation, and the usual forms of this group (Drehschmidt and its modifications) can be adapted for the purification of the air entering, so that no sulphur is introduced by it. For scientific use, where accuracy is of first importance, the Drehschmidt type would have considerable advantage; but for commercial work this increase in accuracy is not necessary. In fact it is more than overbalanced by the greater inconvenience of the apparatus as compared with the forms of the Referees type.

If an apparatus of the Referees type be desired, as will usually be the case, there are three common forms from which selection can be made, viz, Referees, Elliott, and Hinman-Jenkins. Each of these three has its peculiar advantages, and it is not possible to combine all of these in any one composite apparatus, nor is one of the three superior to the other two for all purposes.

For use in traveling inspection work the Hinman-Jenkins apparatus is certainly most convenient, since when taken down it can be packed in a very small case and is then easily portable. It is also somewhat more satisfactory in that the condensation of sulphur by the ammonium hydroxide used in it seems to be more certain and perfect than by ammonium carbonate. However, this advantage is lost unless fresh ammonia is added frequently. This frequent addition of ammonia (every 20 to 30 minutes) makes this apparatus less convenient than that of the Referees or Elliott, since it can not be left to run unattended for such long periods as those.

When the gas is burned at 1.0 to 1.2 cubic feet per hour in the Elliott apparatus, it is possible to get a full test within one and one-half or two hours of the beginning of the test. This is perhaps the most rapid-working apparatus of the three, but it requires a larger bulk of wash water, and it is also rather large and clumsy. The increase in size over the Referees form is a distinct advantage if a rapid rate of burning of the gas is desired, but it is not at all certain that in the end anything is gained by this increase in rate.

The Referees apparatus is most often used in gas testing in this country, and on this ground alone has some advantage for official use, since a result obtained with a form of apparatus in very general use is more generally accepted than a result from another form less well known. This general use of the Referees apparatus has been justified by its simplicity, convenience, and accuracy; and, although the accuracy obtainable with this as well as with other forms has often been overestimated, yet the results are quite satisfactory for all commercial or official work if reasonable care is observed in the selection and operation of the instrument.

2. PRECAUTIONS IN SELECTION OF APPARATUS

The observance of a few simple precautions in selection of the apparatus will perhaps prevent great inconvenience or even serious error in later work. It is therefore desirable to call attention here to a few of the most frequent difficulties in order that they may be avoided more easily.

Hinman-Jenkins.—This form of apparatus is supplied as far as we know by only one apparatus company [8] and is made by them to correspond very well with the original specifications. The dimensions of the various parts are given in the description and the apparatus is illustrated in an earlier section of this paper (p. 10). We recommend that the original form be followed exactly, since this has been found by us, as well as by several State inspectors, to be very satisfactory. However, it would be preferable to have the beads used in the condenser solid and not perforated, since the washing of the latter form is necessarily less efficient; and the bead jar should be filled to within 1 inch of the top with these beads (it is often only half filled). The burner should give a clean-cut blue flame and when burned at ordinary pressure (1.5 to 2.5 inches of water) should pass about 0.5 cubic foot of gas per hour. The proper adjustment of the burner is important, since otherwise incomplete combustion of the gas may result from leakage of the gas unburned from the air holes at the base of the burner.

Referees.—The description and figure of the Referees apparatus previously given do not give exact dimensions of the apparatus, for the reason that the different makers are supplying apparatus of somewhat different sizes, all of which will be satisfactory if within the limits set in this description. However, some of the essential points on which difference in form makes real difference in the convenience or reliability of the apparatus may be indicated. The trumpet tube must not be connected with the condenser by a rubber adaptor or stopper; the form of cork stopper previously indicated is very easily adjusted and is satisfactory. (See p. 6.) If a lead or other metal plate is furnished as a support for the marbles, it should be replaced by a glass rod bent into S shape. The drip tube should extend up into the base of the condenser about one-sixteenth of an inch, in order to keep a layer of liquid over the rubber stopper at the bottom.

Elliott.—The most recent form of apparatus described by Dr. A. H. Elliott [9] should be slightly modified by sealing the trumpet tube to the U tube connecting with the first condenser, since a rubber joint at this point introduces great liability to error. The

[8] L. E. Knott Apparatus Co., 15 Harcourt Street, Boston, Mass.

[9] Described above, as given in a private communication to the Bureau of Standards.

burner may be an ordinary metal Bunsen burner or, as described by Dr. Elliott, a porcelain Bunsen burner. The latter is cleaner and more attractive in appearance, but is fragile, expensive, and less likely to be so well made as to burn only 1 cubic foot of gas per hour without striking back when the flame is nonluminous. As is shown by the Referees burner, a metal burner can be used with entire satisfaction, and this is true even when no lava tip is used. The dimensions given previously (p. 8) are those of the originator's selection; if a smaller apparatus is desired it can easily be used, but the rate of burning the gas would then need to be reduced.

3. DIRECTIONS FOR SETTING UP OF APPARATUS.

If any form of apparatus except that of the Drehschmidt type is used, it is necessary for accurate work that it be set up in a room where no other gas is being burned in order that the air entering the apparatus may be free from sulphur. This will ordinarily cause no inconvenience. The apparatus can be readily set up in the office room of the inspector instead of in the chemical laboratory, since a simple gas connection is the only piping needed and the operation of the instrument need cause no objectionable dirt or odor.

The apparatus consists of pressure governor, U-water gauge, meter, and sulphur apparatus, these being connected in the order given. If the gas used for the sulphur test is also used for the ammonia test, the ammonia absorber is connected between the source of gas supply and the pressure governor. For connecting the various parts of the apparatus rubber tubing is not satisfactory for two reasons. First, the rubber can absorb and give up sulphur from and to the gas according to the quantity of sulphur in the gas and the temperature; and, second, the rubber tubing soon becomes hard and is much more apt to leak than is a metal or a glass tube. It is most convenient usually to make the connections from governor to gauge, gauge to meter, and meter to burner permanent; these can be of glass tubing with rubber connections wired on, except the connection of meter to burner. For the latter it is best to solder a metal tube to the burner inlet (about 6 to 8 inches is a convenient length), so that if the burner strikes

back during a test the connection is not broken at the base of the burner and gas allowed to escape or take fire at this point. Especially for long runs, when no one is in the room for a long time during the test, such a connection is much safer than one of rubber.

The meter and governor used may be either of the wet or dry type. The usual precautions as to leveling and proper adjustment should, of course, be observed. The pressure on the governor should be so adjusted once for all that when the gas is turned on full at the supply cock the burner will pass gas at the desired rate.

The connection between meter and burner, as well as the meter itself, should be frequently tested to show the absence of leaks. Any leaks, even very small ones, may cause appreciable errors in the test, since the rate of gas consumption is small.

4. METHODS OF OPERATION RECOMMENDED

After all connections and adjustments of the apparatus have been made the gas should be burned from the apparatus for several hours to saturate the meter and governor water and to purge the connections. Before each test the line may be purged in this way by burning the gas for about a half hour, a burner which will pass 5 cubic feet or more per hour being substituted for the regular test burner.

When the line is thus purged, the regular burner is put in place and ammonia or ammonium carbonate placed on the burner; for the Referees and Elliott apparatus as much ammonium carbonate is used as will find place about the burner pillar, and for the Hinman-Jenkins about 10 cc of strong ammonia solution is used. The ammonium carbonate should be in large lumps which have been freed from efflorescent portions.

It is usually desirable to rinse out condenser and chimney tubes just before starting the test, in order to prevent dust which might have collected there between tests contaminating the condensate. This also prevents loss of sulphur from the dry condenser during the first few minutes. When all parts, including the flask to collect the condensate are in place, the trumpet tube is set over the burner and quickly connected with the condenser, the meter read-

ing being noted at the instant the trumpet tube is put in place. This reading and the time, meter temperature, barometer, and manometer readings are recorded in the test record book.

The gas being burned at one-half cubic foot per hour in the Referees or Hinman-Jenkins or 1 foot in the Elliott apparatus, the test can be continued for any desired period, the ammonia or ammonium carbonate being renewed, as indicated below. If the sulphur in the condensed liquid is to be determined by means of a turbidimeter (see a later section of this paper), it is necessary to burn the apparatus only two hours. In this event it is not necessary to renew the ammonium carbonate for either the Elliott or Referees apparatus; but in this or any other test about 3 or 5 cc of fresh ammonia solution must be added to the Hinman-Jenkins apparatus every 20 minutes.

If the sulphate is to be determined gravimetrically, it is generally desirable to burn at least 2½ or 3 cubic feet of gas for a test. However, there is no need for burning 10 feet, as usually is done, since the gravimetric method is sufficiently accurate on the sulphur from 2.5 feet of ordinary coal gas or water gas to give no error as great as the irregularities of condensation in the apparatus. These are not appreciably lessened by longer runs. The advantage of burning the gas over a long period in order to get a so-called "better average sample of the gas" is much overestimated. With the ordinary uniformity of works operation and a single coal supply, changes in the sulphur content of the gas from day to day are very small. For this reason a short test will usually give as fair a sample of the full day as one taken over a long period.

When it is desired to burn more than 3 cubic feet of gas for a test, it is necessary to replenish the supply of ammonium carbonate on both the Elliott and the Referees' apparatus. To do this the gas is shut off and the trumpet tube allowed to cool so that it may be handled comfortably. A fresh supply of carbonate is then added, the burner relighted, and the trumpet tube replaced quickly. If more than a very few thousandths of a cubic foot of gas are burned with the trumpet tube off, the amount so burned should be deducted from the total used for the test. A fresh supply of carbonate must be added in this manner after every 3

feet of gas burned in either the Referees or Elliott apparatus; with the Hinman-Jenkins apparatus ammonia is added every 20 minutes.

When sufficient gas has been burned, the supply is cut off and the apparatus allowed to cool. The trumpet tube is then washed once and the condenser four times. For the Referees and Hinman-Jenkins apparatus each portion of wash water is 50 cc and is added all at once to thoroughly flush the condenser; with the Elliott form 100-cc portions of water are used, the last two portions used in the second tower being subsequently used as the first two portions for the first tower. In this way the wash water is kept at reasonable bulk. The time, meter reading, meter temperature, and barometer are recorded again at the close of the test.

The sulphate in the condensed liquid and wash water is determined by one of the methods given in a later section of this paper. From sulphate found and corrected volume of gas burned, the sulphur content of the gas (in grains of sulphur per 100 cubic feet of gas) is calculated.

IV. DETERMINATION OF SULPHATE IN THE SOLUTIONS OBTAINED

In all the forms of apparatus described, the suplhur is obtained in solution in the form of sulphates and, except in the case of the Somerville procedure, it is this sulphate which must be determined. The oxidation from sulphites to sulphates is accomplished in the Drehschmidt and Somerville types of apparatus by an oxidizing agent, usually bromine or iodine, in the absorption liquid; and in the other forms of apparatus it is accomplished by the action of the oxygen in the hot products of combustion on the alkaline solution of sulphite formed in the condenser.

Numerous determinations were made of the sulphites present in the condensate from the various forms of apparatus and, while it was nearly always possible to get a qualitative test for sulphites, the amount was never found to be in excess of two-tenths of a per cent of the total sulphur present. It is, therefore, a negligible amount in a determination of this kind.

The methods of determining the sulphate which are available for use for this work are of three kinds—gravimetric, volumetric, and turbidimetric. The procedure used for most of the comparisons described in the previous sections was the first gravimetric method described below (practically the one recommended by Johnston and Adams;[10] but for some of the comparisons of Table 10 the turbidimetric procedure was followed.

In the following sections four methods are given which have been tried out with solutions of the character obtained from the Referees type of apparatus, together with a short series of comparisons which shows that they are sufficiently accurate for this kind of work.

1. METHOD I—GRAVIMETRIC, WITH EVAPORATION TO DRYNESS

Dilute or evaporate the portion of liquid taken for analysis to about 300 cc, add 50 cc of concentrated hydrochloric acid, heat to boiling, then run in 10 cc of 10 per cent barium chloride solution through a tube or from a burette, delivering it at the rate of about 8 to 10 cc per minute, stirring constantly during the addition. After evaporation to dryness on the steam bath, take up with 75 to 100 cc of hot water, filter through a good, close-grained paper, and wash with hot water until the bulk of the filtrate and washings amounts to 200 cc. In a weighed platinum crucible char the paper with a low Bunsen flame and finally ignite until the precipitate appears white. Cool the crucible in a desiccator and weigh.

The precipitate now contains a small amount of silica, which may cause an error of 0.1 to 0.4 grain per 100 cubic feet in the apparent amount of sulphur in the gas. Bearing this source of error in mind, it is only necessary to correct for it when the amount of sulphur exceeds the legal limit by a small amount. The correction is easily made by moistening the precipitate with a drop of hydrofluoric and then one of sulphuric acid, drying, igniting, and weighing again. The silica is all removed by this operation.

[10] J. Amer. Chem. Soc., 33, pp. 829–845; 1911.

2. METHOD II—GRAVIMETRIC PRECIPITATION IN NEARLY NEUTRAL SOLUTION

In the more common procedures for the gravimetric sulphate determination, the precipitation of the barium sulphate is made in nearly neutral solution. This method was used by us as follows:

To the solution which is diluted or concentrated to about 300 cc, add 2 or 3 drops of methyl-orange or p-nitrophenol solution[11] and neutralize with hydrochloric acid, adding this solution dropwise; and finally add 2 cc of the 1 : 1 acid in excess. Heat to boiling, add 10 cc of 10 per cent barium chloride solution, boil five minutes, allow to stand on a steam bath for a half hour or longer, filter, wash, ignite, and weigh the barium sulphate as in Method I. The precipitation when always made in the presence of a fixed amount of acid is affected always in equal degree by the solubility of the barium sulphate in the acid. Under the conditions given the loss from this source is negligible for the present work.

3. METHOD III—VOLUMETRIC

A number of volumetric methods have been recommended for the determination of sulphates, several of which are suitable for use with the liquids obtained from the Referees' and Hinman-Jenkins apparatus. Only one of these, a modification of that recommended by Holliger,[12] will be described.

Make up a solution of 50 g $BaCl_2.2H_2O$ per liter, and one of 30.5 g $K_2Cr_2O_7$ per liter. To 300 cc of water add 10 cc of 1.1 hydrochloric acid and exactly 15 cc (from pipettes) of each of the above solutions; heat to boiling, add two or three drops of a dilute solution of ferric chloride, then slowly add 10 per cent ammonium hydroxide until a precipitate forms, which does not redissolve on stirring. Add 5 cc of the ammonia solution in excess, boil five minutes, filter and wash thoroughly with hot water. Allow the filtrate to cool, acidify with hydrochloric acid, add 2 grams of solid potassium iodide, or a solution containing that amount, and titrate with tenth normal sodium thiosulphate, using starch as an indicator. The amount of thiosulphate solution used in this

[11] Any other indicator sensitive to ammonia, but not affected by carbon dioxide, may be used.
[12] Z. anal. Chem., 49, p. 84, 1910.

blank is to be subtracted from the amount used in each subsequent determination.

To make a determination of the sulphate in a solution, dilute or concentrate the sample taken to 300 cc, add 10 cc of 1.1 hydrochloric acid, heat to boiling, add 15 cc of barium chloride solution from the pipette used in the blank test, boil five minutes, add 15 cc of potassium bichromate solution and a few drops of ferric chloride, precipitate with ammonium hydroxide, and complete the determination exactly as in the blank test. From the amount of thiosulphate solution used subtract the amount required in the blank. The remainder represents the sulphate in the sample taken.

The reactions upon which the method is based are:

$BaCl_2 + H_2SO_4 = BaSO_4 + 2HCl$

$BaCl_2 + K_2CrO_4 = BaCrO_4 + 2KCl$

$2K_2CrO_4 + 16HCl + 6KI = 6I + 10KCl + 2CrCl_3 + 8H_2O$

$2I + 2Na_2S_2O_3 = Na_2S_4O_6 + 2NaI$

From the above equations it will be seen that three $Na_2S_2O_3$ are equivalent to one S; hence 1 cc of tenth-normal thiosulphate solution is equivalent to 1.069 mg (0.0165 grain) of sulphur.

The above method was selected in preference to other methods previously used, which have been open to the following objections:

1. In those using a hydrochloric acid solution of barium chromate the reducing action of the acid on the chromate has introduced serious errors.[13]

2. In those which use exactly equivalent amounts of barium chloride and potassium bichromate, it is somewhat difficult to make the solutions of exactly the right strength and a blank test must be made.[14]

3. The use of a suspension of barium chromate or of the solid is less convenient than that of solutions and since it is sometimes difficult to obtain the barium salt free from alkali chromate a blank test should also be made with this method.[15]

---

[13] Andrews: Am. Chem. J., **11**, p. 567; 1889. Pennock: J. Am. Chem. Soc., **26**, p. 1265; 1903. Holliger: Zs. anal. Chem., **49**, p. 84; 1910. Bradley: Chem. Eng., **13**, p. 26; 1911. Reuter: Chem.-Ztg., p. 357; 1898.

[14] Roemer: Zs. anal. Chem., **49**, p. 490; 1910. Precht: Zs. anal. Chem., **18**, p. 521; 1879.

[15] Bruhns: Zs. anal. Chem., **45**, p. 573; 1906. Kowarowsky: Chem.-Ztg., p. 498; 1907.

4. In all methods, the solubility of the barium chromate should be taken into account.

All of these sources of error or difficulty are taken care of by a single blank test, when the chromate solution is slightly stronger than the barium chloride solution, as in the method described. The solubility of barium chromate is somewhat affected by the concentration of ammonium chloride and of ammonium hydroxide in the solution; but by having the same bulk of solution, adding the same amount of hydrochloric acid, and precipitating in the same manner in the blank as in the determination, the effect of this source of error is also eliminated. The use of a small amount of ferric chloride, as recommended by Holliger (loc. cit.), aids greatly in collecting the precipitate of $BaCrO_4$ and $BaSO_4$ for the filtration.

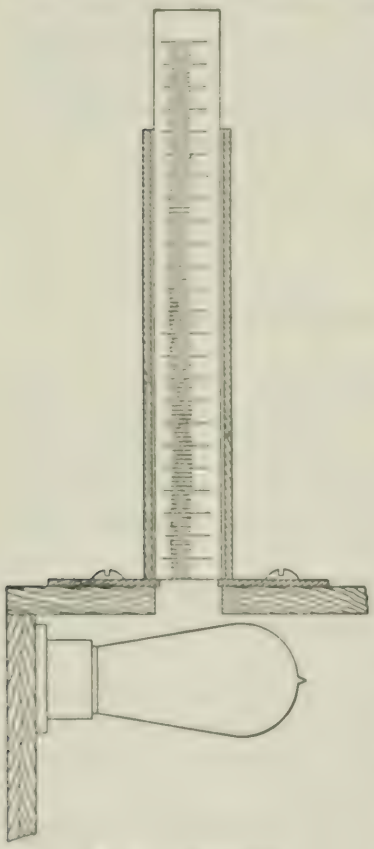

Fig. 9.—*Turbidimeter*

4. METHOD IV—TURBIDIMETRIC

An investigation to determine the suitability of the turbidimeter[16] as a means of estimating sulphur in the solutions from the Referees apparatus, and the effect of varying certain conditions was undertaken. In all, about 300 determinations were made. The turbidimeter used is shown in Fig. 9. It consists of a cylindrical glass tube graduated from the bottom in centimeters, surrounded and held in place above the light by a brass tube. The light used was in most cases a 16-candlepower carbon filament lamp, so placed that a straight portion of the filament extended diametrically across just below the bottom of the tube.

[16] [illegible] J. Am. Chem. Soc., 18, [illegible] 22, [illegible] 24, [illegible] 1902.

For each determination the sulphate is precipitated with barium chloride and the solution stirred vigorously until precipitation appears to be complete. It is then poured into the tube until the filament entirely disappears, the depth of solution required to cause this disappearance being a measure of the amount of sulphate in the solution.

Since little was known of the effect of different conditions of operation on the result of the tests, a number of special comparisons were made, the results of which are given in the following paragraphs.

The incandescent filament gives a sharper end point than any other source of light so far devised.[17] It is not affected by drafts, does not smoke or crack the tube, and can be conveniently placed under a table or in another out-of-the-way place. A series of comparisons, using the incandescent filament, the standard candle, and the 0.5 mm slot recommended by Leighton (loc. cit.), is given in Table 11. In each case the same liquid was used with each source of light in turn. It can be seen that the three light sources give excellently agreeing results.

TABLE 11

Comparison of Results with Different Lights in Turbidimeter

Incandescent filament		Candle		Electric light below a 0.5 mm slot	
Depth of solution	Milligrams of sulphur per 100 cc	Depth of solution	Milligrams of sulphur per 100 cc	Depth of solution	Milligrams of sulphur per 100 cc
24.0	1.13	25.0	1.12	25.0	1.12
20.3	1.22	20.6	1.21	20.4	1.22
12.3	1.77	12.3	1.77	12.2	1.79
11.6	1.86	11.8	1.85	11.6	1.86
8.5	2.48	8.5	2.48	8.4	2.51
7.2	2.93	7.0	3.01	7.2	2.93
5.9	3.60	6.1	3.50	5.9	3.60
5.4	3.95	5.4	3.95	5.2	4.09
4.1	5.25	4.1	5.25	3.9	5.55
3.7	5.93	3.8	5.77	3.7	5.93
3.4	6.50	3.5	6.26	3.3	6.70

[17] See Jackson: J. Am. Chem. Soc., **23**, p. 799; 1901. Parr: J. Ind. Eng. Chem., **1**, p. 689; 1909. Leighton, U. S. Geological Survey Water Supply and Irrigation Paper No. 151, p. 27; 1905.

See also H. F. Muer: J. Ind. Eng. Chem., **3**, p. 553–7; 1911. This article reports an extended series of tests on the turbidimeter.

The effect of using different precipitants as proposed by various persons who have used the turbidimeter for sulphate determinations is shown in Fig. 10. It will be observed that there is less

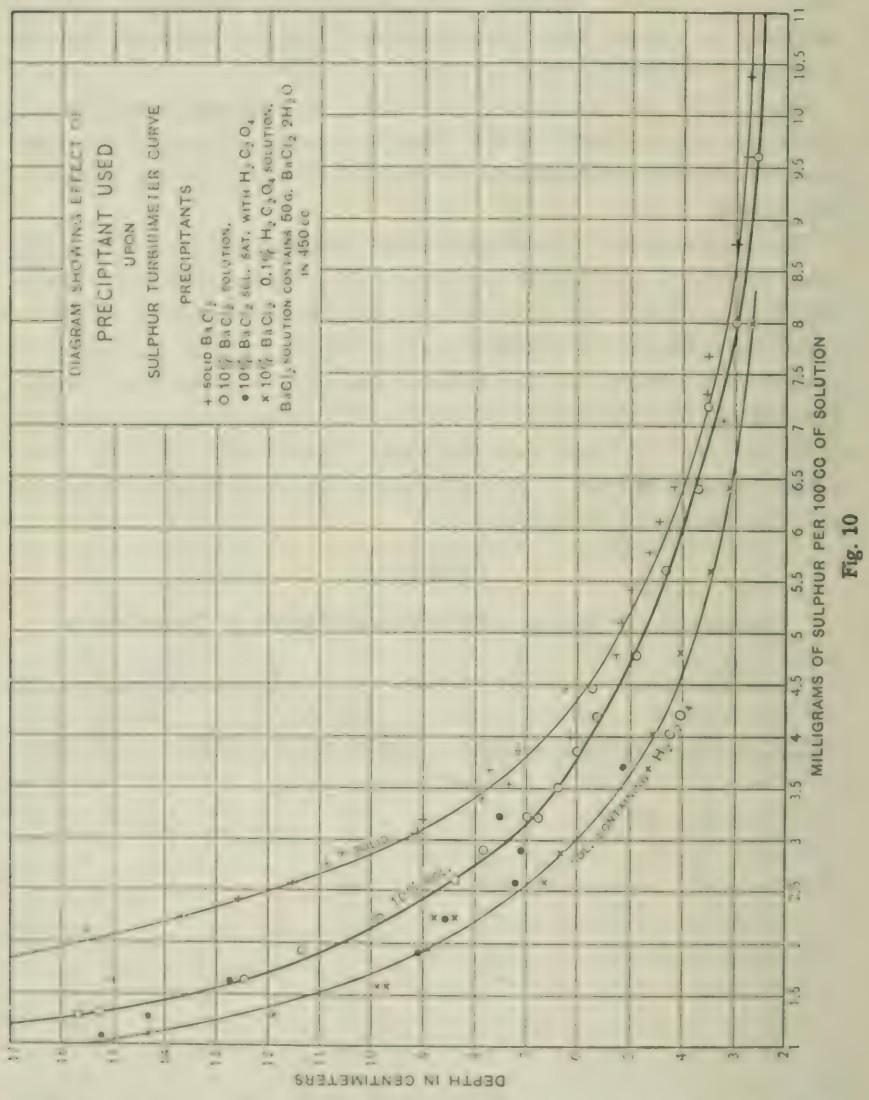
DIAGRAM SHOWING EFFECT OF
PRECIPITANT USED
UPON
SULPHUR TURBIDIMETER CURVE
PRECIPITANTS
+ SOLID $BaCl_2$
○ 10% $BaCl_2$ SOLUTION.
• 10% $BaCl_2$ SOL. SAT. WITH $H_2C_2O_4$
× 10% $BaCl_2$ 0.1% $H_2C_2O_4$ SOLUTION.
$BaCl_2$ SOLUTION CONTAINS 50 G. $BaCl_2 \cdot 2H_2O$ IN 450 CC
MILLIGRAMS OF SULPHUR PER 100 CC OF SOLUTION
DEPTH IN CENTIMETERS

Fig. 10

variation where 10 per cent barium chloride solution is used than with other precipitants; the addition of oxalic acid gave a finer precipitate and a sharper end point, but successive determinations

were more discordant. Agreement of duplicates and certainty of result is most desirable in this method, since in any case the results are fixed by comparison with results on known amounts of sulphur. Variation of a single test from the average of all is therefore serious, but the shape of the calibration curves is not of influence, so long as regular and calibration tests are made in the same way.

Fig. 11 shows the effect of small amounts of hydrochloric acid upon the turbidimeter curve. Larger amounts caused much greater variations. Fig. 12 shows the effect of temperature of precipitation upon solutions of average strength. Fig. 13 is the curve drawn from the results obtained under the conditions of precipitation recommended below. Fig. 14 represents the same data as Fig. 13, with concentrations expressed in hundredths of a grain instead of milligrams.

The following method was finally adopted, and is recommended for use if it is desired to employ a turbidimetric procedure:

The condensate and washings from the sulphur apparatus are neutralized with hydrochloric acid,[18] then 2 cc of the 1:1 acid is added in excess. The solution is measured (to the nearest cubic centimeter) and a 90-cc portion placed in a small beaker for the test. It may be measured in an ordinary graduated cylinder if it is certain that the ratio of the small cylinder to the larger measuring vessel first used is correct. While the solution is between 25 and 30°, 10 cc of a 10 per cent solution of $BaCl_2.2H_2O$ is added and the whole stirred vigorously until the precipitation appears to be complete. (This usually requires less than one minute's stirring.)

The suspension is now poured into the clean and dry turbidimeter tube, a small portion at a time, until the filament of the lighted lamp disappears from view. After the first trial the solution is poured back into the beaker, stirred vigorously, and the observation of the point at which the filament disappears is repeated until this is fixed within 1 mm. During the time the solution is being added the portion remaining in the beaker should be kept well stirred, so that the small portions added from it will be representative of the whole bulk. The first time the solution is poured into the observation tube the latter must be dry and

[18] An indicator is required which is sensitive to ammonia but not to carbon dioxide. Para-nitro-phenol is the most satisfactory because it is colorless in acid solution.

clean. In cleaning it care should be taken to remove, without scratching the tube, the film of sulphate which adheres so persistently to the bottom.

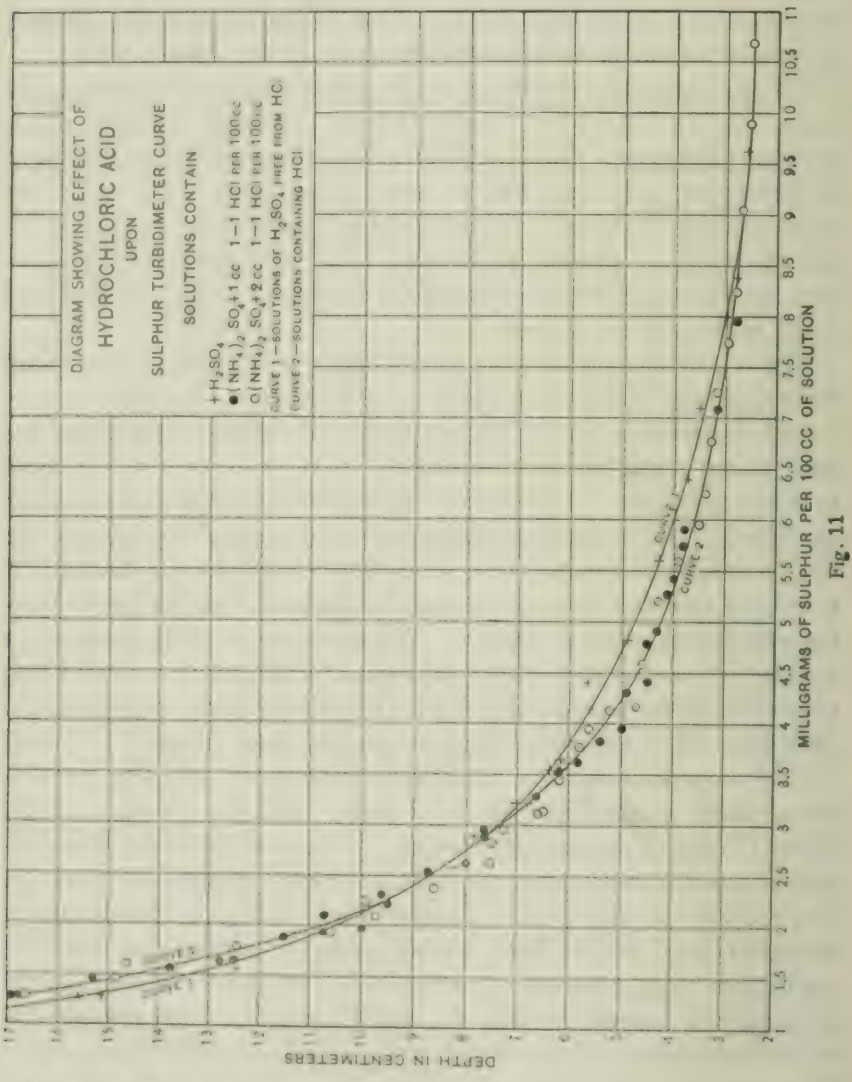
DIAGRAM SHOWING EFFECT OF
HYDROCHLORIC ACID
UPON
SULPHUR TURBIDIMETER CURVE
SOLUTIONS CONTAIN
+ H_2SO_4
● $(NH_4)_2SO_4$ + 1 cc 1—1 HCl PER 100 cc
○ $(NH_4)_2SO_4$ + 2 cc 1—1 HCl PER 100 cc
CURVE 1—SOLUTIONS OF H_2SO_4 FREE FROM HCl
CURVE 2—SOLUTIONS CONTAINING HCl
MILLIGRAMS OF SULPHUR PER 100 CC OF SOLUTION
DEPTH IN CENTIMETERS
CURVE 1
CURVE 2

Fig. 11

Further tests on a second 90 cc of the original neutralized solution of sulphate should be made if considerable accuracy is needed. The amount of sulphur indicated by the curves of Figs. 13 and 14,

corresponding to the depth of liquid in the turbidimeter measurement, is multiplied by the number of cubic centimeters of neutralized condensate and divided by 90 (the volume of sample taken) to give the total amount of sulphur obtained by burning the gas.

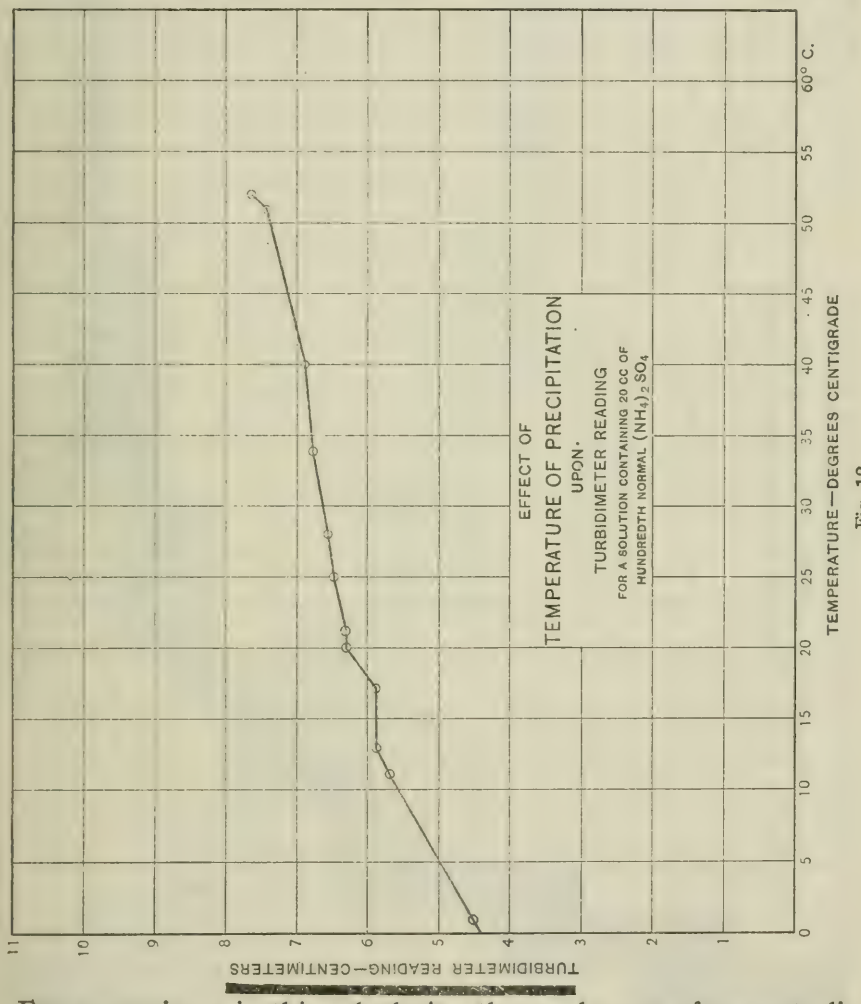
EFFECT OF
TEMPERATURE OF PRECIPITATION
UPON
TURBIDIMETER READING
FOR A SOLUTION CONTAINING 20 CC OF
HUNDREDTH NORMAL $(NH_4)_2SO_4$
TURBIDIMETER READING—CENTIMETERS
TEMPERATURE—DEGREES CENTIGRADE
0 5 10 15 20 25 30 35 40 45 50 55 60° C.
1 2 3 4 5 6 7 8 9 10 11

Fig. 12

For convenience in this calculation the condensate after neutralization can be made up to 270 or 360 cc, and the observed values for the 90-cc portion are then multiplied by 3 or 4.

The curves of Figs. 13 and 14 may be used by any observer if care is exercised in following exactly the method given in the

preceding paragraph; the acidity and temperature limits must be particularly observed; the character of light used is less important. In any case it is well for an inexperienced observer to take

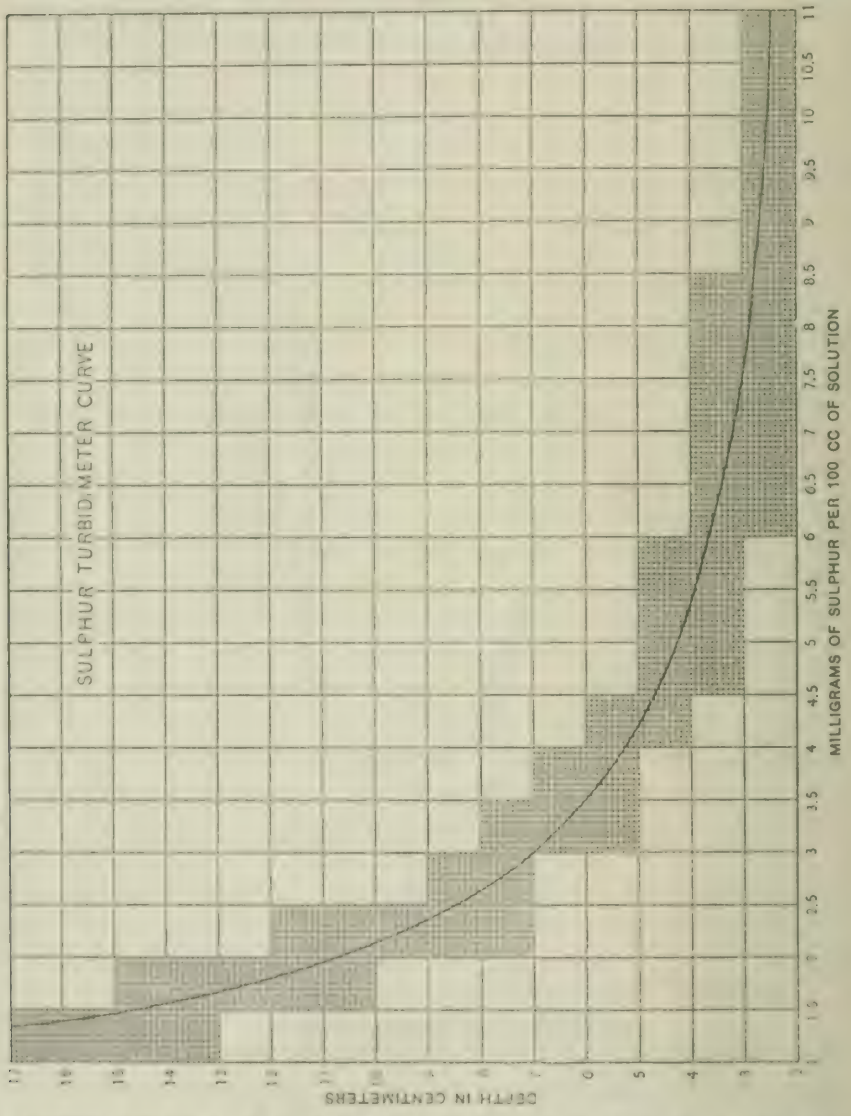

Fig. 13

known amounts of a standard sulphuric acid solution and run through the test until assured that his observations are consistent and correct.

To show the accuracy of the method as used, one series of tests from which our conclusions are drawn has been summarized in Tables 12 and 13. This summary shows the average and the

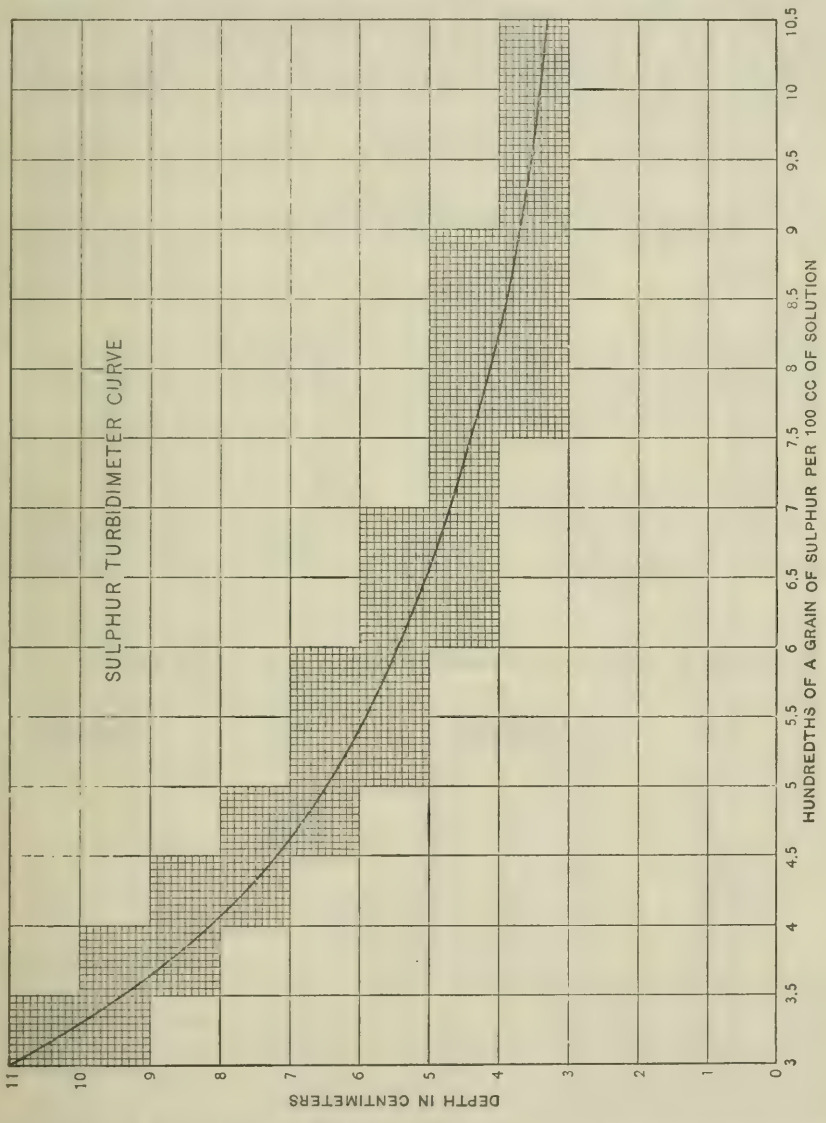

Fig. 14

maximum deviation of individual tests from the value calculated from the amount of standard sulphuric acid used—i. e., the errors which were found by making a single precipitation of barium sul-

phate and suitable observations on it. When more than one portion is precipitated and used for a determination, the accuracy would be materially increased, so that in tests on three portions of a solution the average of the three ought not to be much more than 1 per cent in error. It should be remembered that three tests can be made in this way much more quickly than a single test by any other method.

TABLE 12

Turbidimetric Errors

Sulphur	Average error	Maximum error	Number of determinations
Mg per 100 cc	*Per cent*	*Per cent*	
1– 2	2.9	8.7	13
2– 3	3.5	7.1	13
3– 4	2.5	7.7	17
4– 5	2.6	6.3	8
5– 6	1.3	5.2	7
6– 8	2.6	5.6	7
8–11	3.4	6.3	5
All values.....	2.7	8.7	70

TABLE 13

Percentage of error in determinations between 2 and 8 mg per 100 cc

Error	Number of determinations	Error	Number of determinations
Per cent		*Per cent*	
0.0–0.5	11	5.5–6.5	1
0.5–1.5	12	6.5–7.5	2
1.5–2.5	5	7.7	1
2.5–3.5	7		
3.5–4.5	3	Total.....	52
4.5–5.5	5		

5. COMPARISON OF METHODS FOR THE SULPHATE DETERMINATION

For the present purposes it was sufficient to know that the several methods for the sulphate determination gave results agreeing within 1 per cent; but under the conditions of their use, on solutions containing considerable amounts of ammonium carbonate, it was not certain that this was the case. However, a number of comparisons which we have made show that the agreement of the four methods among themselves is satisfactory. All of the details of these tests are not given here; only sufficient data are included to show that these simple methods are suitable for our purpose.

TABLE 14

Comparison of Methods for Sulphate Determination. Sulphur (Milligrams per Gram of Solution) in Standard H_2SO_4 Solution Determined by Different Methods in Presence of Excess of Ammonium Carbonate, except as Otherwise Noted

Volumetric, against NaOH and benzoic acid	Gravimetric, method 1	Gravimetric, method 2	Volumetric, method 3	
			Oxalate standard (no carbonate added)	H_2SO_4 standard
1.589	1.591	1.597	1.602	1.595
93	91	93	1.597	1.602
90	90	92	1.600	1.597
92	[19] 1.609	99	1.599	1.601
92	1.596	97	1.602	1.596
92	96	92	.....	1.589
89	88	99	.....	1.574
90	92	91	.....	1.575
.....	94	1.600	.....	.....
1.591	1.592	1.595	1.600	1.589

[19] Omitted from average.

The data of the above table show the results obtained under rather unfavorable conditions by the two gravimetric and the one volumetric method as compared with the correct values obtained for a standard sulphuric acid solution by a usual and accepted procedure. The results of the first set by method 3 are

calculated on the basis of the value of the thiosulphate solution obtained by titration against potassium permanganate, which was standardized with sodium oxalate. In the second series the thiosulphate was checked against the standard sulphuric acid itself; in this latter the tests were made in the presence of added ammonium carbonate. The values given were in some cases obtained on very small amounts of sulphate, from 6 to 30 mg of sulphur being present in the various test samples. The results are thus less precise than otherwise and do not give very fair credit to the method as far as its possible accuracy goes.

For accurate work the gravimetric methods are to be preferred, but for rapid work the turbidimetric and volumetric methods will serve very well, and, unless the test indicates that the sulphur is very near the permissible limit, they are probably sufficiently accurate for official use. The volumetric method is adapted especially for use in state inspection, where a large number of test solutions are collected in the field work and subsequently examined at the headquarters laboratory. In most cases, however, the turbidimeter, which is easily portable, may be carried with the inspector and a test made at the time the sulphate is collected, thus avoiding the necessity of transporting the solutions obtained to headquarters.

WASHINGTON, March 7, 1913.

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No. 21

DEHYDRATION OF CLAYS

BY

G. H. BROWN, Assistant Ceramic Chemist
and
E. T. MONTGOMERY, Laboratory Assistant
Bureau of Standards

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By G. H. Brown and E. T. Montgomery

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I. INTRODUCTION

1. STATEMENT OF THE PROBLEM

Upon ignition the hydrous silicates of alumina, of the general type $Al_2O_3.2SiO_2.2H_2O$, which form a greater or smaller part of the pure and impure clays, lose their combined water within a certain temperature range. With this dissociation the character of the clays changes in an important manner. The property of plasticity is greatly diminished and may even be completely destroyed and deep-seated molecular transformations occur which are indicated by a decrease in specific gravity, increased solubility in acids and alkalies, and other decided alterations.

2. EARLIER INVESTIGATIONS

Until recently the dehydration temperatures of clay were not known with any degree of exactness. Le Chatelier [1] assumed a series of ranges which depended upon the structure of the substance, varying from 150 to 770° C. Kaolin he supposed to

[1] Zs. physik. Chemie, 1, p. 396; 1887. Comptes Rendu, 104, pp. 1443, 1517.

dehydrate at 770°, a value considerably too high in the light of later measurements. Depending upon the dehydration ranges, Le Chatelier attempted a classification of clay like hydrous minerals, distinguishing five classes of substances, but examination of his lag curves would seem to indicate that this procedure is based upon very slender evidence.

An American investigator, Ellis Lovejoy,[2] determined the ignition loss of a No. 2 fire clay at the melting points of different metals and found the dissociation temperature to be near the fusion point of antimony, about 630°. Another American, A. E. Barnes,[3] as the result of similar work, reported the decomposition as taking place at about 565°. W. M. Kennedy,[4] under the direction of Edward Orton, jr., carried on a series of weighings of brickettes made from Florida kaolin, 30 grams in weight, at temperatures up to 1000° C. Here loss of combined water was clearly shown to have taken place at 475°. The chemical study of dehydrated kaolin received attention by Hillebrand,[5] F. W. Clarke,[6] McNeil,[7] Knote,[8] and others. Hillebrand described a sample of pure crystalline kaolinite and stated that none of the water escapes at 330° C. The water was considered by this investigator to be probably basic water.

Clarke mentions that "after dehydration at low redness kaolin is completely decomposable by hydrochloric acid, but the ignited mass contains no silica soluble in sodium carbonate solution." The complete decomposition of dehydrated kaolin was confirmed by McNeil. Knote, upon treating Kentucky flint clay heated to 600° C and 1000° with hydrochloric acid, found that the material ignited to the lower temperature yielded an extraction of 44 per cent, while the more highly calcined clay resulted only in the solution of 5 per cent. The relation between calcination temperature and solubility was studied more closely by Sokoloff, to whose work reference will be made later.

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[2] The Clay Worker, 1888.
[3] The Clay Worker, **23**, p. 505, June, 1895.
[4] Trans. Am. Ceram. Soc., **4**, p. [illegible], 1902.
[5] U. S. Geol. Survey, Bull. **20**, p. 98, 1885.
[6] Ibid., Bull. **125**, p. 30.
[7] J. Am. Chem. Soc., **28**, p. 691.
[8] Trans. Am. Ceram. Soc., **12**, p. 226, 1910.

3. RECENT INVESTIGATIONS

Knote,[8] in a research on fire clays, showed by means of specific-gravity curves that a sudden increase in volume occurs between 450° and 500° which reaches a minimum at 550° in the case of a plastic clay and at 600° with a Kentucky flint clay. For most clays, however, the point was found to be located at 550°. Beyond this temperature the density increased gradually up to 900°, when, between this temperature and 950°, a more or less rapid decrease in specific volume occurred. As regards the density drop at 550°, Knote suggests that the $Al_2O_32SiO_22H_2O$ breaks up to form $Al_2O_3SiO_2 + Al_2O_33SiO_2 + 4H_2O$, a reaction which is not very probable. The rise in density at 950°, accompanying an exothermic transformation, was noted by Le Chatelier and by him ascribed to the polymerization of alumina.

The increase in volume coincident with dehydration has been noted by several earlier investigators. Lovejoy[9] noted that during this stage a decided expansion took place in bricks which he measured.

H. E. Ashley[10] summarized the facts known with reference to dehydration and reported some determinations of the dehydration range of a number of clays made in the clay products laboratory of the Bureau of Standards at Pittsburgh.

In heating clay an initial slow rate of heating was noted, due to the water held by the colloidal clay up to 300°. A retardation was then observed from 500° to 575°, due to the expulsion of the combined water. Following this stage a second retardation from about 825° to 925° and an acceleration occurring at about 925° were detected. The acceleration is the same which was previously found by Le Chatelier.[11]

An investigation dealing with this subject has been reported by J. W. Mellor and A. D. Holdcroft.[12] The temperature range of the decomposition of kaolin was determined, and it was found that dehydration begins at no fixed temperature, but that the decomposition is appreciable at 500°. A marked lag appeared only

[8] Trans. Am. Ceram. Soc., **7**.
[9] J. Ind. and Eng. Chem., **3**, pp. 91–95; February, 1910.
[10] See footnote 1.
[11] Trans. Engl. Ceram. Soc., **10**, pp. 94–120.

between 600° and 700°. At about 900° the exothermic reaction was noted. The specific gravity of kaolin was reduced from 2.615 at 110° to 2.489 at 700°. Kaolin heated to 700° was found to be more soluble in hydrochloric acid than the untreated material. The above investigators conclude from the evidence obtained that upon dehydration the molecule breaks up into free silica, free alumina, and water. The exothermal change, it is claimed, corresponds to a physical change of the free alumina whereby the latter becomes less soluble in acids, less hygroscopic, and more dense. A certain parallelism exists in the properties of alumina and calcined kaolin. (This does not agree with the results obtained by Sokoloff and his assistants.) On the basis of somewhat incomplete evidence Mellor and Holdcroft assume that the OH and Al groups are symmetrically placed in the molecule. Upon heating dehydrated kaolin under steam pressure these investigators succeeded in restoring 3 to 4 per cent water.

An extensive research upon the dehydration of clays was carried on by R. Rieke,[13] who sought to determine the differences in the dehydration temperatures of kaolins and clays, the possibility of definite dissociation temperatures and the loss of combined water at different temperatures. It was found by means of heating curves that heat absorption was observable at temperatures as low as 425° with some clays. The beginning of a pronounced halt, however, was never noted below 510° and for the average of 10 kaolins this point was about 538°. The lag extended to about 580° in most cases. Similar results were obtained with fire clays. The loss of weight increases rapidly with the temperature, since the velocity of the dissociation increases greatly as the temperature rises. Again, it was found that the decomposition was not completed at 700° after long continued heating, there remaining almost 0.5 per cent to be driven off at a still higher temperature. Rieke found that plasticity was not necessarily destroyed upon dehydration. No evidence was produced which tended to show an unsymmetrical arrangement of the OH groups.

This question was likewise studied by A. M. Sokoloff [14] with special reference to the readiness with which the kaolin molecule

[13] Sprechsaal, **44**, pp. 617–641, 653–656. [14] Tonindustrie Zeitung, **36**, 1107–1111.

is decomposed by a hot hydrochloric-acid solution. Upon heating kaolin for five hours at different temperatures the following results were obtained:

Temperature	Loss in heating	Per cent soluble Al_2O_3
°C	Per cent	
400	3.85	.....
500	11.70	28.99
600	.....	33.74
700	12.94	33.96
800	13.00	34.67

The molecular ratio Al_2O_3:H_2O for all temperatures approaches 1:2 quite closely.

II. EXPERIMENTAL WORK

The present study was undertaken for the purpose of comparing a number of typical American clays as regards the following relations: (1) Dehydration temperature range; (2) loss of weight upon heating at constant temperatures; (3) specific gravity after heating to several temperatures; (4) loss of plasticity due to heating to several temperatures.

The clays examined in this work were as follows: No. 1, kaolin from North Carolina; No. 2, kaolin from Georgia; No. 3, ball clay No. 3 from Tennessee; No. 4, a second-grade fire clay from Union Furnace, Ohio; No. 5, a plastic fire clay of good grade from Mount Savage, Md.; No. 6, flint clay from Mount Savage, Md.; No. 7, a ferruginous shale from Cleveland, Ohio; No. 8, a paving-brick shale from Galesburg, Ill.; No. 9, highly plastic surface clay from Curtice, Ohio; No. 10, plastic surface clay from Columbus, Ohio.

1. DEHYDRATION TEMPERATURE RANGE

Owing to the fact that dehydration is an endothermic reaction, a more or less distinct lag is to be expected upon heating specimens of the clay. The determinations under consideration were made by comparing the heating curve of an electrically heated furnace with that obtained by measuring the temperature within a clay cylinder. The furnace temperature was read by means of a

thermocouple, that of the interior of the clay cylinder by means of a resistance coil and a Leeds and Northrup bridge suitable for this work. The heating coil consisted of a chrome-nickel wire around the interior of the furnace, which was 5 inches long and 2 inches in diameter.

The test specimens, which weighed about 30 grams, were dried at 110° C, until constant in weight, when they were heated to 200° before being placed in the furnace. In Figs. 1 and 2 the heating curves of the clays are shown, together with the time-temperature curve of the furnace, which follows a straight line obtained by close regulation of the current. Taking up the clays in their order the following observations were made:

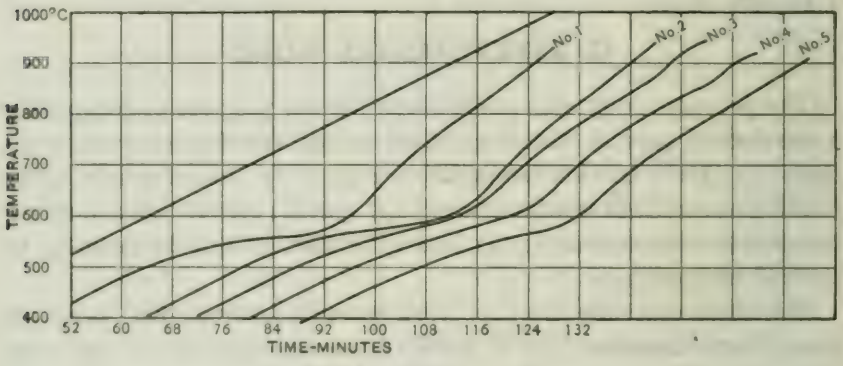

Fig. 1.—*Heating curves*

No. 1. North Carolina Kaolin.—This clay shows a marked retardation, first distinguished at about 480°, the main heat absorption being between 540° and 570°. The loss in weight of the clay at 650° was 13.20 per cent. The exothermic change below 850° is clearly marked.

No. 2. Georgia Kaolin.—The heat absorption becomes evident with this clay at 525° and the lag is prominent between this temperature and 590°, covering a period of 24 minutes. At 650° the loss in weight was 12.93 per cent. In this case also the heat evolution appears to start at 850°.

No. 3. Tennessee Ball Clay.—Retardation becomes manifest at 510° and the lag extends to 600°, with a period of about 20 min-

utes. Exothermic acceleration not so well marked as in preceding clays. Loss in weight, 10.67 per cent at 650°.

No. 4. Ohio Fire Clay.—Lag begins at 520° and is not as well defined as for the purer clays. It is most evident between 550° and 600°. The loss in weight at 650° is 6.69 per cent. The exothermic transformation is observed more faintly than in the preceding materials.

No. 5. Maryland Fire Clay.—Lag begins at 480° and extends over a considerable period of time and temperature range. The retardation is most pronounced at 580°. The loss in weight at 650° is 5.68 per cent. The acceleration between 850° and 900° is decidedly faint.

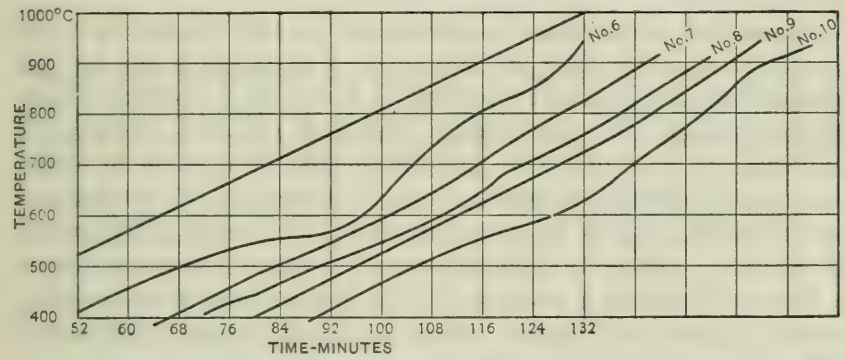

Fig. 2.—*Heating curves*

No. 6. Maryland Flint Clay.—A pronounced retardation is shown by this material already recognizable at 450° and most evident between 550° and 575°. The loss in weight was 10.45 per cent at 650°. The exothermic reaction is particularly well shown between 870° and the final temperature.

No. 7. Ohio Shale.—A slight lag is observed which is first recognized at 485°. The loss in weight at 650° is 3.98 per cent. Owing to the various factors affecting the weight of the clay, such as the oxidation of the carbon and ferrous oxide, dissociation of pyrites, etc., the weight after heating can not be considered a reliable expression of the combined water loss. At 880° the acceleration of the curve is distinctly noticeable.

No. 8. Illinois Shale.—Lag not well defined, though extending over a considerable period of time. It is distinctly recognized at 480° and may be traced up to 670°. An acceleration is noticed beyond 850°. In impure clays of this type it is difficult to determine whether changes of this kind are to be ascribed to the exothermic reaction of Le Chatelier or to the combustion of the small quantities of carbon. The loss of weight at 650° was found to be 4.88 per cent.

No. 9. Ohio Surface Clay.—No lag is shown in this curve, but the acceleration is observed. The loss in weight was 5.63 per cent.

No. 10. Georgia Surface Clay.—The lag is first observed at 490° and becomes quite noticeable at 600°. The loss in weight was 10.09 per cent.

Comparison of the diagrams brings out clearly the fact that the combined water of the clay substance is expelled at no definite temperature but leaves throughout a fairly long continued temperature range. We are dealing, therefore, not with compounds analogous to pure hydrates, but rather with substances in which the water is held only in part as water of hydration. The distinctness of the lag, as is to be expected, affords a criterion of the purity of the clay. Water is expelled before a lag in the heating curves is shown, though at a slow rate. The acceleration in the heating curve at about 850° seems to be most pronounced in the clays higher in combined water; that is, clays of the purer types.

2. LOSS OF WEIGHT UPON HEATING

In the study of the quantitative course of dehydration it was decided to use the loss in weight as the measure of decomposition. From the exact standpoint, of course, it would be far more desirable to determine the residual combined water directly by the standard methods employed for this purpose. Since, however, the main object of the work was to ascertain the rates of loss and the critical temperature range, the direct estimation of the fixed water was not considered necessary.

In this part of the work specimens of clay, weighing about 10 grams, were used. They were dried at 110° to constant weight and then heated to 200°, 400°, 450°, 500°, 550°, 600°, 650°, and 700°, until practically constant in weight: i. e., when the loss in

TABLE 1

Loss of Weight in Per Cent After Heating for 4 to 6 Hours at Indicated Temperatures

Clay	200°	400°	450°	500°	550°	600°	650°	700°	800°	1000°
1	0.42	1.76	2.20	11.50	12.45	12.65	13.20	13.37	13.99	14.00
2	0.21	0.77	2.16	11.64	12.42	12.52	12.93	13.18	13.42	13.46
3	1.44	1.86	4.88	9.90	10.35	10.53	10.67	11.02	11.20	11.20
4	0.10	1.59	3.60	5.35	6.25	6.58	6.69	6.88	6.99	7.25
5	0.30	1.30	2.37	5.01	5.23	5.49	5.68	5.81	5.84	6.00
6	0.30	1.09	4.28	9.36	9.84	10.15	10.45	10.68	10.77	10.95
7	0.32	1.20	1.74	3.00	3.51	3.72	3.98	4.13	4.27	4.57
8	0.24	1.26	2.50	3.80	4.14	4.86	4.88	5.06	5.27	5.47
9	1.33	2.83	3.54	4.31	5.13	5.36	5.63	5.65	5.76	6.07
10	1.25	3.13	5.98	9.14	9.57	9.86	10.09	10.04	10.62	10.64

a two-hour period did not exceed 0.2 per cent. The results of this work are compiled in Table 1 and are shown graphically in Figs. 3 and 4. From the diagram it appears at once that there

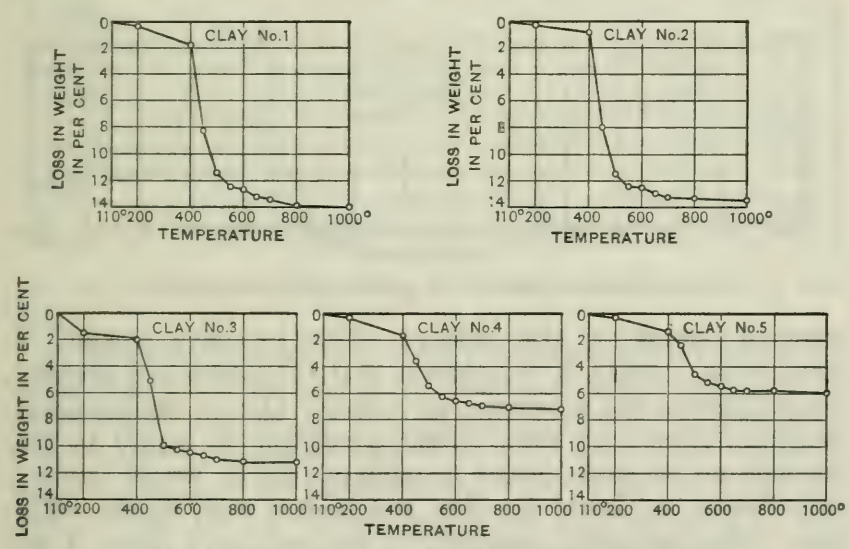

Fig. 3.—*Diagram showing loss in weight at different temperatures*

are, roughly, three stages in the evolution of the combined water. Some loss occurs at temperatures up to 400°, but at a comparatively slow rate. Between this temperature and 500° the rate

of loss is greatly accelerated. Above 500° the loss of combined water is again retarded so that the expulsion of the last portions proceeds slowly. This diagram further affords a sharp classification of the various clays, according to their purity, based obviously on the contents of combined water. In this manner three groups of clays are differentiated—kaolin, fire clay, and impure clays. An interesting fact brought out is the presence of a surface clay in the middle group. This may be explained by the fact that this particular material is a Georgia clay of the ball clay type,

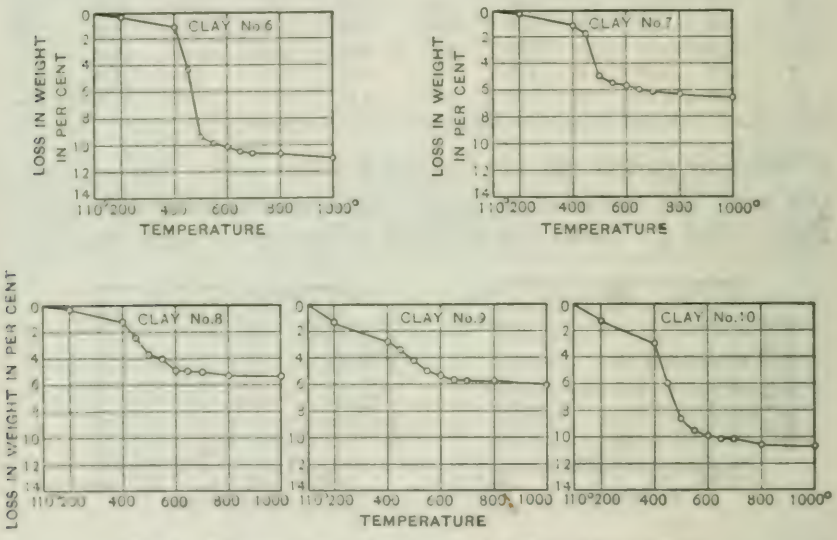

Fig. 4.—*Diagram showing loss in weight at different temperatures*

rendered impure by the presence of an excessive amount of ferric oxide. Again, it is apparent that the kaolin and fire-clay groups possess clay substance very closely akin in mineralogical structure, since both show strong parallelism in regard to the temperature range at which maximum loss in weight occurs. The shales, the impure fire clay, and surface clay, on the other hand, differ decidedly, inasmuch as the loss curve covers a far wider range of temperature, and for this reason we are justified in assuming that the clay substance represents another type of material. The statement commonly made that the plastic sub-

stance of all clays is of the same type, therefore, is in error. Attention must again be called to the fact that the loss in weight does not represent the true loss of combined water, owing to the changes occurring in connection with the combustion of the carbon, the oxidation of ferrous iron, the dissociation of pyrite, and the decomposition of calcium carbonate. These factors evidently are more pronounced in the impure clays than in the purer ones. However, the variations thus introduced are not sufficient to overthrow the general result as regards the essentially different

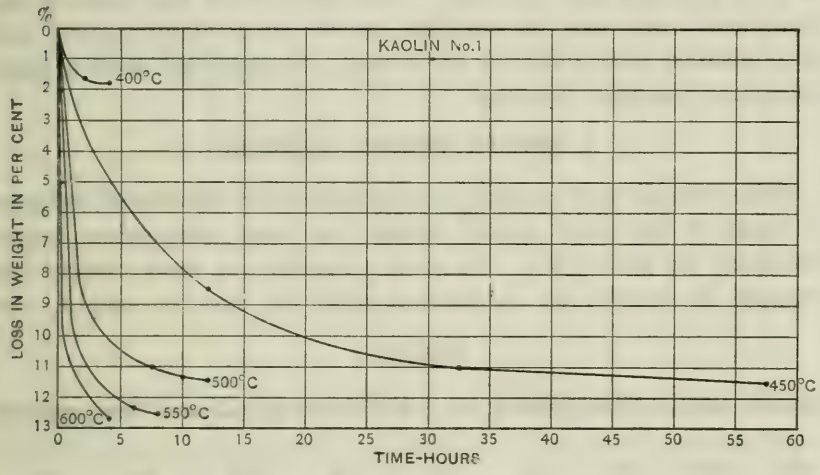

Fig. 5.—*Diagram illustrating rate of loss in weight*

rate of dissociation prevailing for the ferruginous clays and shales.

An interesting feature of the dehydration process is the difficult elimination of the last portions of combined water. It is observed that at about 550° the rate of dehydration slows up very markedly. It is found, for instance, that with N. C. kaolin the chemical water expelled at 550° represents but 1.672 of the two molecules of H_2O, while for the Georgia kaolin and the Maryland flint clay these amounts are 1.73 and 1.795 molecules, respectively. This fact points out the necessity for thorough ignition to insure the complete dehydration of clay, and in addition seems to indicate a firmer union of the remaining portion of the water with the

kaolin molecule than is shown by the part leaving between 450° and 550°. The rate of loss upon heating 10-gram pieces of kaolin is shown in the diagram of Fig. 5, from which it is seen that the velocity of the reaction increases rapidly with the temperature, but that it slows down as the curve approaches the amount of maximum loss. Thus, after four hours of heating the losses in weight were as follows: 1.75 per cent at 400°, 5 per cent at 450°, 10.1 per cent at 500°, 11.8 per cent at 550°, and 12.7 per cent at 600°. The run at 450° was carried on for 57½ hours and a loss of 11.5 per cent was reached. This shows that the bulk of the combined water can be expelled at the lower temperatures and it is possible that even all of it might be removed after a long-continued period of heating.

3. SPECIFIC GRAVITY CHANGES

This constant was carefully determined upon pulverized samples of eight of the clays heated under the usual precautions found necessary for such work. In order to point out more clearly the changes in density in correlation with the loss in weight, the

TABLE 2

Specific Gravity After Heating for 4 to 6 Hours at Indicated Temperatures

Clay	200°	400°	450°	500°	550°	600°	650°	700°
1	2.600	2.570	2.480	2.440	2.480	2.485	2.490	2.490
2	2.600	2.580	2.520	2.460	2.485	2.490	2.500	2.490
3	2.650	2.640	2.630	2.530	2.590	2.600	2.590	2.600
4	2.720	2.720	2.710	2.570	2.580	2.580	2.580	2.580
5	2.690	2.685	2.650	2.570	2.610	2.605	2.615	2.615
6	2.620	2.600	2.550	2.475	2.500	2.530	2.560	2.580
7	2.790	2.750	2.730	2.720	2.710	2.700	2.710	2.710
8	2.740	2.750	2.750	2.730	2.715	2.715	2.700	2.705
9	2.755	2.765	2.730	2.700	2.690	2.690	2.670	2.675
10	2.625	2.650	2.565	2.555	2.595	2.610	2.615	2.625

curves showing the latter are replotted. The numerical results of the work are shown in Table 2 and are presented graphically in Figs. 6 and 7. As is to be anticipated, the purer clays show a much more marked decrease in density—i. e., increase in volume—

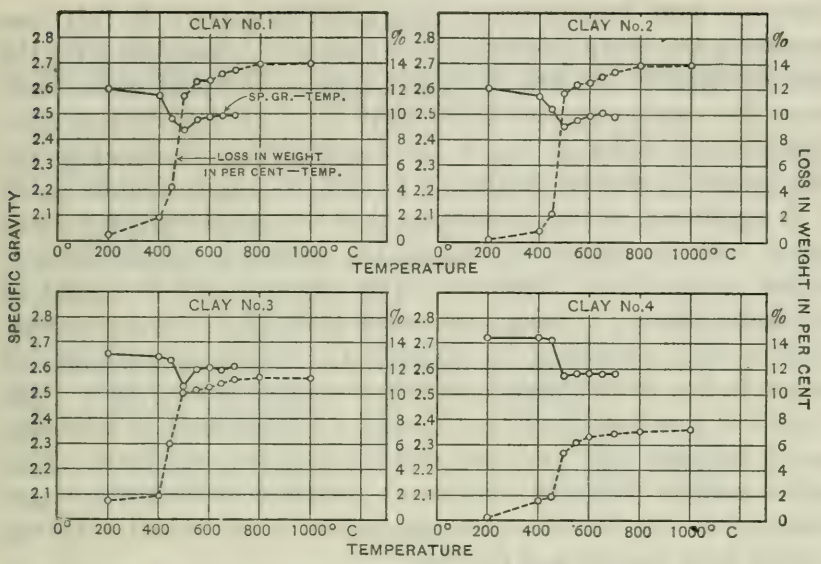
CLAY No.1
CLAY No.2
CLAY No.3
CLAY No.4
SP. GR.—TEMP.
LOSS IN WEIGHT IN PER CENT—TEMP.
SPECIFIC GRAVITY
LOSS IN WEIGHT IN PER CENT
TEMPERATURE
0° 200 400 600 800 1000° C
% 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1
14 12 10 8 6 4 2 0

Fig. 6.—*Diagram showing specific gravity and loss in weight at different temperatures*

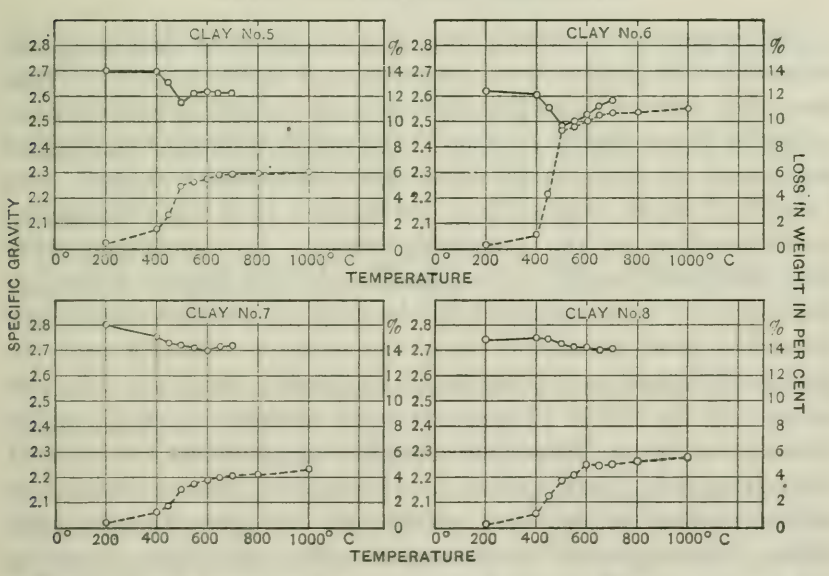
CLAY No.5
CLAY No.6
CLAY No.7
CLAY No.8
SPECIFIC GRAVITY
LOSS IN WEIGHT IN PER CENT
TEMPERATURE
0° 200 400 600 800 1000° C
% 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1
14 12 10 8 6 4 2 0

Fig. 7.—*Diagram showing specific gravity and loss in weight at different temperatures*

than the more impure ones. The interesting point in this connection is the sharp minimum shown at 500°, coincident with the greatest drop of the loss in weight curve. It would seem, then, from the specific gravity curve that the true dehydration temperature, the point at which the vapor tension is equal to the atmospheric pressure, might be located at approximately 500°. It is significant in this connection that the specific gravity curve shows such a decided reversal at the minimum point, which is rather unexpected. With the more impure clays the point of minimum density is recognized more difficultly or is not emphasized at all. According to Sokoloff, the maximum solubility of kaolin in hot hydrochloric acid is not reached before 700°. This condition is retained until 800°, when a sudden drop in solubility occurs between 800° and 900° and the clay becomes inert. It is quite evident that the exothermic reaction or transformation observed in the time-temperature curves is coincident with the sudden inert condition of the clay.

4. RESIDUAL PLASTICITY OF CLAYS

In this part of the work cylindrical specimens of clay, weighing from 80 to 90 grams, were prepared and dried at 110°. These were then heated to practically constant weight at several temperatures in an electric furnace. The pieces were then pulverized and made up again with water into cylindrical shapes. The volume of these were at once determined in a volumenometer, using kerosene as the measuring liquid. The specimens were then dried and heated at 110°, upon which the volume was again determined. It was desired to show at what temperatures the clays lost their plasticity, using the working behavior and the drying shrinkage as a criterion of the plastic condition. In this connection the initial plastic state was subject to certain variations owing to the difficulty of establishing a uniform condition of consistency for all specimens. This condition became more difficult to control as the clays approached the granular nonplastic state. The numerical results are compiled in Tables 3 and 4.

TABLE 3

Drying Shrinkage, in Per Cent of Dry Volume, After Preheating to Indicated Temperatures

Clay	Air dry	110°	350°	400°	450°	500°	550°	600°	650°	700°	750°	800°
1	16.42	16.28	20.20	16.15	12.58	11.97	12.48	11.90	.....	.....	.....	.....
2	19.69	19.30	15.98	13.44	9.34	7.86	6.11	6.94	.....	.....	.....	.....
3	42.70	38.02	22.12	14.08	8.16	9.75	7.33	8.03	.....	.....	.....	.....
4	18.55	18.67	14.25	14.80	10.89	12.59	12.50	11.67	.....	.....	.....	.....
5	18.70	16.20	14.60	13.82	13.50	14.42	13.23	11.12	.....	9.97	10.12	7.94
[15]6	8.17	8.78	7.87	8.78	5.44	6.40	5.58	.....	.....	.....	.....	.....
7	17.29	17.18	14.56	14.03	13.83	16.08	15.62	13.72	11.25	9.30	7.26	.....
8	15.30	14.78	12.92	13.28	13.21	15.23	14.22	13.70	10.42	9.58	9.26	5.82
9	44.30	39.50	11.93	9.46	8.89	8.37	7.72	7.40	.....	.....	.....	.....
[16]10	37.40	36.55	13.70	11.12	7.55	4.78	.....	.....	.....	.....	.....	.....

[15] At 600° test pieces crumbled. [16] At 550° test pieces crumbled.

TABLE 4

Water of Plasticity, in Per Cent of the Dry Weight, After Preheating to Indicated Temperatures

Clay	Air dry	110°	350°	400°	450°	500°	550°	600°	650°	700°	750°	800°
1	32.32	32.03	38.48	37.90	42.39	46.83	46.66	48.67	.....	.....	.....	.....
2	32.33	32.22	32.56	31.60	34.83	36.85	37.30	38.65	.....	.....	.....	.....
3	47.40	44.50	38.50	36.65	40.30	44.20	42.70	46.70	.....	.....	.....	.....
4	21.35	21.40	19.65	21.38	22.35	24.70	26.45	26.92	.....	.....	.....	.....
5	22.65	22.20	21.40	22.18	24.56	25.97	26.80	27.10	26.42	25.30	26.55	28.58
6	15.30	15.28	16.78	17.43	19.70	22.00	22.18	23.80	.....	.....	.....	.....
7	20.99	21.25	21.67	22.08	24.55	25.20	25.92	25.65	26.20	25.73	28.80	.....
8	24.65	23.45	23.50	23.85	24.23	28.25	28.95	30.15	29.00	28.92	30.70	32.20
9	35.48	34.68	28.25	28.80	28.45	30.83	31.75	33.55	.....	.....	.....	.....
10	39.55	36.85	32.20	34.80	37.20	38.55	42.40	39.52	.....	.....	.....	.....

The several clays showed peculiarities in behavior after preheating which are summarized as follows:

No. 1. North Carolina kaolin.—After preheating to 110° the plasticity was found to be the same as that of the air-dried sample. Upon heating to 350° a slight decrease in plasticity was observed which was apparently not diminished by carrying the temperature to 400°. At 450° a considerable decrease in the plastic behavior was observed, the clay becoming granular in structure.

This condition became more marked by heating to the higher temperatures.

No. 2. Georgia kaolin.—Preheating at 110° caused a slight decrease in plasticity. A quite noticeable decrease occurred at 350° which was slightly more marked at 400°. At 450° another decided change toward the nonplastic condition took place and the granular structure became apparent as in clay No. 1. At 650° and 700° there was no further change. A significant loss in plasticity was caused by heating at 750°, and at 800 the plasticity was entirely destroyed.

No. 3. Tennessee ball clay, No. 3.—This clay appeared to suffer a slight decrease in plasticity at 110° over that of the air-dried sample. At 350° a decided decrease in plasticity was observed, the clay being no longer "sticky," but having the working qualities of a No. 2 fire clay. At 400° there was a further large loss of the plastic quality, the clay assuming the granular structure observed in the two kaolins when heated to 450°. Heating at 450° developed a granular, sandy structure.

No. 4. Fire clay of second grade.—The plasticity of this clay was not materially decreased when heated to a temperature below 450°. At this point the material suffered a decided decrease in plasticity, although it still retained a fair working property. At 500° an additional loss on plastic behavior was noted, a condition not changed by heating to 550°. A somewhat granular structure was developed at 600°.

No. 5. Plastic fire clay.—Only a slight decrease in plasticity was noted upon heating to 350° with no further change caused by carrying the temperatures to 400° and 450°. The clay appears somewhat granular upon first adding water but the plastic state is rapidly developed. This condition persists at 500° and with practically no further change at 550°. At 600° an appreciable decrease is noted, although the material is still quite plastic. Smaller losses in plasticity are observed at 650° and 700°. At 750° the clay lost its ability to be molded.

No. 6. Flint clay.—The initial plasticity of the flint clay was small and decreased slightly with the temperature of heating. The test pieces could not be molded after heating to 600°.

No. 7. Shale.—At 110° there was no appreciable decrease in plasticity over that in the air-dried condition. At 350° there appeared to be a slight increase in plasticity as is shown by the improved molding properties. At 400° the working quality was bettered still more and no further change appeared to take place at 450°, 500°, and 550°. A very slight decrease in plasticity was observed at 600°, a condition somewhat emphasized at 650° and 700°. A large decrease in plasticity occurs at 750° and the working properties are destroyed.

No. 8. Shale.—The behavior of this shale is similar to that of No. 7, the plasticity being retained without decrease at temperatures below 650°.

No. 9. Surface clay.—This clay is exceedingly "sticky" and dries with difficulty. When preheated at 110° no decided change in plasticity was noted. At 250° the material loses its stickiness and has improved working qualities. At 300° there is a further reduction in plasticity and at 350° this property is entirely destroyed, the structure becoming granular. This condition is not changed by heating at the higher temperatures.

No. 10. Surface clay.—This clay also possesses excessive plasticity and is decidedly "sticky" in its nature. No reduction is caused by heating at 110°. At 250° the stickiness disappears and the working quality is improved. A further decrease in plasticity occurs at 300°. Heating at 350° develops a granular structure with poor working properties. At 400° and higher temperatures the plasticity is destroyed.

In the diagrams of Figs. 8 and 9 the volume shrinkage and water contents of the clays after preheating at the several temperatures are shown. It appears from the shrinkage curves that the plastic clays are far more sensitive to the heat treatment than are the less plastic ones, while the shales show surprising resistance and even seem to become more plastic at 350° to 400°. Excessively plastic clays become more workable at the latter temperatures and their rate of drying seems to be increased. The order in which the working plasticity of the several types of clays is destroyed is as follows: Surface clays, 400°; ball clay, 450°; kaolins, 600° and 500°, the more plastic one being affected more

than the one less so; No. 2 fire clays, 600° and 750°; shales 750° and 800°. By comparing the shrinkage with the working behavior it is apparent that the former is by no means a criterion of the plasticity and does not express the effect of the granular structure caused by the agglomeration of the clay mass. Upon examining the water content of the clays after preheating, Fig. 9, it is shown that a more or less pronounced break occurs in the water content at 350° and 400°, with 9 of the 10 clays. Beyond this point the

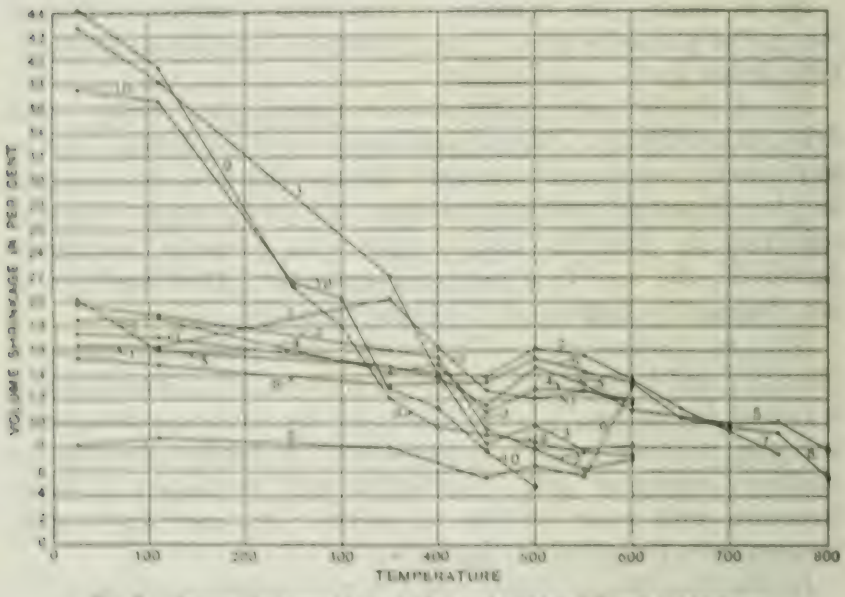

Fig. 8.—*Volume shrinkage of clays after preheating to different temperatures*

amount of water required to produce a mass which can be molded increases decidedly and may be equal to or greater than the weight contained in the natural plastic clay. Part of the water added penetrates more deeply into the clay structure to replace the so-called hygroscopic or absorbed water and even a portion of the combined water which has been expelled. In addition it would fill the space previously occupied by any organic matter which has been volatilized or oxidized, and a portion no doubt is used to occupy the larger pore space of the clay caused by agglom-

eration. A study of the distribution of the water as shrinkage, pore and residual water would undoubtedly be more valuable in correlating the loss in plasticity than the determination of volume shrinkage.

There can be no doubt but that the more or less pronounced break in the water content curve represents a critical temperature at which significant changes in the clay structure takes place. The production of a granular structure in the case of the plastic

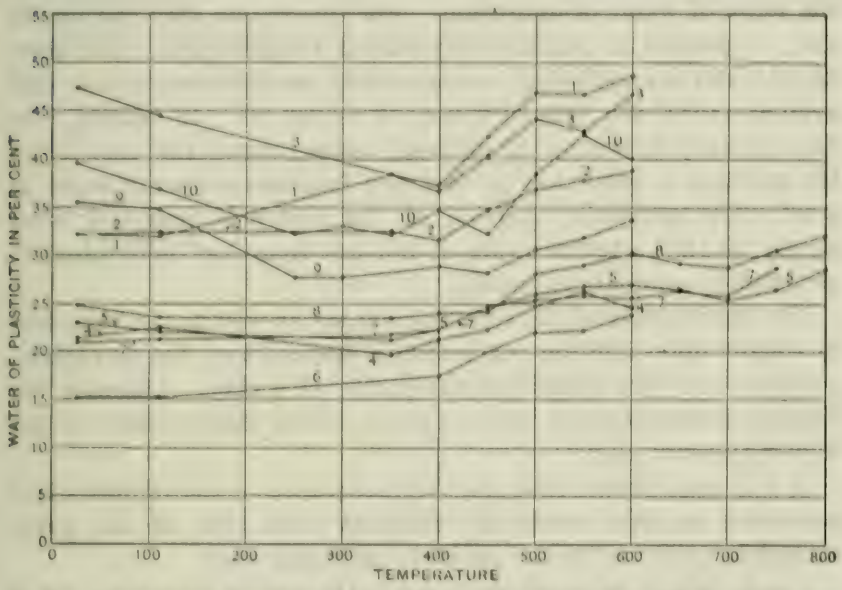

Fig. 9. *Water required to produce plastic condition after preheating to different temperatures*

clays and the expulsion of the hygroscopic moisture are closely connected with this transformation. At 500°, at which temperature one should expect some significant changes, none are apparent except in the shrinkage curves where a number of the clays show a more or less marked maximum, to which, however, in the face of the possible variations in the water content, no special importance can be attached.

This work seems to prove also that the presence of organic compounds is not a primary factor in the property of plasticity

since shales show good plastic qualities after heating to temperatures at which without question the carbon is completely burnt out. There can be no doubt that organic material has an important influence upon the plasticity of clays, but it is of a supplementary rather than a fundamental character.

III. SUMMARY

All of the combined water of clay is not part of the clay base in the sense of water of hydration. For this reason clay can not be said to possess a definite dehydration temperature. The combined water is expelled at comparatively low temperatures so that even at 450° C the bulk of it may be driven off. In heating clay to constancy in weight at different temperatures the velocity of the reaction is very slow at first and becomes suddenly rapid at 500°. The remaining portion of the water is removed more slowly, so that a temperature of not less than 800° is required to accomplish complete expulsion.

The distinctness of the endothermal lag as well as the total loss in weight upon ignition (excluding abnormal loss due to carbon, sulphur, etc.) are criteria of the purity of a clay. Likewise the thermal acceleration at about 850° is shown more clearly by the higher types of clay.

It has been shown that the clay substance of the impure clays represents a type essentially different from that of the purer materials, contrary to the generally accepted view.

A well-defined minimum is shown in the specific gravity curve of clays, located at approximately 500°.

Dehydration does not necessarily destroy the plasticity of clays, and hence the combined water appears to have no direct connection with the phenomenon of plasticity. Shales are least affected by heating within the dehydration temperature range, and in fact seem to be improved in plastic working behavior after preheating to about 500°. The surface clays examined lose their plasticity at the lowest temperatures, about 400°, followed by ball clay, at 450°, kaolin 500° to 600°, No. 2 fire clays 600° to 750°, and shales 750° to 800°.

It was likewise shown that the presence of organic compounds can not be a primary cause of plasticity, since these are oxidized in an atmosphere of pure air at about 500°. It was shown quite clearly that drying shrinkage is not a true criterion of plasticity, contrary to the statement of Rohland, who makes the claim that this contraction is the best measure of the property in question.

In connection with this work the writers wish to express their indebtedness to Mr. A. V. Bleininger for assistance in reviewing the results.

WASHINGTON, April 25, 1913.

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No. 22

EFFECT OF OVERFIRING UPON THE STRUCTURE OF CLAYS

BY

A. V. BLEININGER, Ceramic Chemist

and

E. T. MONTGOMERY, Laboratory Assistant

Bureau of Standards

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By A. V. Bleininger and E. T. Montgomery

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I. INTRODUCTION

1. CAUSE OF VESICULAR STRUCTURE

Clays, like rocks of all kinds, contain considerable amounts of gaseous constituents in the form of dissociable compounds, occluded and dissolved gases. During the firing constant evolution of gas takes place. In the earlier stages the hygroscopic water is expelled as steam, followed later by the combined water of the clay substance, carbon dioxide from the combustion of carbon, and the dissociation of carbonates, sulphur di- and trioxide from pyrites and gypsum, oxygen due to the reduction of ferric oxide. On the other hand, during the firing, absorption of air, hydrocarbons and other gases may occur at times while the temperature is constant or is temporarily lowered.

The firing of clays brings about a decrease in the initial pore space, a process which as it approaches completion is called vitrification. This closing up of the pore space is caused by the softening of the mass and the effect of surface tension which operates to bring about a condition of minimum surface area.

The progress of vitrification then can be followed by means of porosity determinations, provided the structure of the material in question is sufficiently open to allow of the ready escape of the gases evolved. If at any time the evolution of gaseous matter is rapid enough so that pressure is produced within the clay, bloating is certain to take place and a vesicular structure will be formed.

2. OPEN AND INCLOSED PORE SPACE

Assuming that normal conditions prevail and that vitrification progresses steadily, one aspect of the decrease in porosity must receive attention. Starting with maximum porosity immediately after the dehydration of a clay it is found that the total pore space is practically measured by the volume of water absorbed in vacuo. This indicates that the pore system is open and the capillaries communicate with each other. During vitrification some of the fine channels are closed and thus cut off a portion of the pore space. The system therefore is no longer open and must be divided into open and inclosed pore space. Gas evolved within one of the inclosed pores must break its way through the walls in order to escape. Since the viscosity of most clays still remains very considerable, it is readily seen that gas vesicles may be under considerable pressure before they are released, when they leave behind greatly enlarged spaces. Anywhere throughout the clay mass, especially in connection with cavities left during the molding, gas accumulations may occur.

The practice of "oxidizing" the clays, so well presented by Orton in his valuable researches, thus becomes a matter of primary importance. The oxidation stage consists in holding the clay at a practically constant temperature, surrounded by an excess of air, between 750° and 800° C until all of the carbon is consumed, the sulphides are decomposed, and any ferrous oxide is changed to the

ferric form. But even though the oxidation has been completed, clays differ widely as regards their tendency to give off further gases, a condition aggravated by the presence of sulphates which are not completely decomposed during this stage of the burn.

Owing to the fact that the presence of gaseous matter likely to be evolved throughout vitrification is always objectionable, due to the serious effects upon the final structure of the clays, causing a general decrease in strength and impermeability, it is evident that clays containing the smallest amounts of such matter are by far the safest and most valuable ones.

3. VITRIFICATION BEHAVIOR OF CLAYS

It is important, therefore, that methods of testing be employed which bring out clearly the qualities in question. From the practical standpoint this question concerns chiefly dense products like paving blocks, sewer pipe, porcelain, stoneware, etc., where serious harm may be done by the overdevelopment of vesicular structure.

Considered from this standpoint, clays might be divided into the following classes as regards the character of structure developed during the highest burning temperatures:

1. Open structure; no vitrification possible.
2. Sound vitrification, with no immediate development of vesicular structure.
3. Vesicular structure developed before vitrification; sound vitrification impossible.
4. Vesicular structure developed, coincident with or immediately after vitrification.

The first group of materials consists principally of the pure clays kaolins, flint clays, etc., or silicious clays in which the amount of fluxing material is insufficient to bring about vitrification. Owing to the open pores the development of vesicular structure is impossible.

The second group embraces the most valuable and useful clays and represents the best types of paving-brick shales, stoneware clays, and similar materials burning to an impervious structure.

In the third class are represented those shales and clays which show a decided development of vesicular structure before vitrification has been completed. This is especially true of many shales which fail to make satisfactory paving blocks. In the preliminary testing of shales this matter does not receive the attention it deserves, as is indicated by the frequent attempts to use materials of this description in the industry.

In the fourth class, clays are found which either offer the same difficulties as the third group or possess such a short vitrification range that their proper firing under commercial conditions becomes practically an impossibility.

In the development of vesicular structure both the physical constitution of the clay, as regards compactness and fineness of grain, as well as the mode of shaping, are of as great, if not greater, importance than the amount of constituents present which form gases. It is obvious that a silicious clay will be able to release more of the gaseous material than one of dense and close structure. Similarly, a dust-pressed body is more open than a plastic molded one.

II. DESCRIPTION OF WORK

The subject of vesicular structure has received the consideration of several workers. Purdy especially has called attention to its importance in several of his investigations, although actual determinations have been reported only in one paper where a fire clay was made the subject of study.[1]

In the present work six clays were examined and their total and inclosed pore space determined after firing to several temperatures, starting from the point at which good maturity had been reached.

These clays were as follows:

No. 1. Surface clay, weathered shale, Cleveland, Ohio.
No. 2. Surface clay, glacial, Curtice, Ohio.
No. 3. Shale, Galesburg, Ill.
No. 4. Shale, Cleveland, Ohio.
No. 5. No. 2 fire clay, Union Furnace, Ohio.
No. 6. No. 2 fire clay, Kittanning, Pa.

[1] Trans. Am. Ceram. Soc., 13, p. 602.

Each batch of these clays was tempered to uniform consistency, and all the specimens were molded from the same lump, rendered as homogeneous as possible. The molding was done in brass molds and the trial pieces were practically cubes, weighing about 130 grams in the burnt state. The drying was carried on slowly at room temperature. In burning, a constant temperature increase of 20° C per hour was maintained. Due to the use of natural gas this was easily possible and the heating curve proposed was followed very closely. The temperature measurements were made by means of a thermocouple and a Siemens-Halske recording millivoltmeter. Part of the time a second couple was inserted through the back of the kiln in order to check the uniformity of the heat distribution. Cones were placed in each burn.

The cold junctions were kept in glass tubes cooled in ice water. At each of the selected temperatures three trial pieces were drawn for the purpose of checking the results. Upon drawing, the sets of specimens were cooled in a pot furnace previously fired to a red heat.

The trial pieces were then weighed, saturated with water in vacuo, followed by the usual determination of the suspended and wet weights. An average sample of the briquettes was then obtained, which was pulverized for the estimation of the true specific gravity by means of the pycnometer.

From these values the per cent of apparent porosity was calculated from the relation $100\ (W - D) \div (D \div S_1)$. The pore space is expressed here in terms of the true clay volume, viz, dry weight, divided by the true density. Similarly, the per cent volume of the inclosed pore space was reckoned from the following formula:

$$\frac{100\left(\frac{D}{S_2} - \frac{D}{S_1}\right)}{\frac{D}{S_1}} = 100\left(\frac{S_1}{S_2} - 1\right)$$

In these expressions:

D = dry weight of specimen.

W = wet weight.

S_1 = true specific gravity.

S_2 = apparent specific gravity of saturated piece.

The total porosity, of course, represents the apparent pore volume plus the volume of the inclosed pore space, all of the values being expressed in terms of the true clay volume. It is quite evident that the apparent specific gravity of the piece equals the true specific gravity only under two conditions, viz, when there are no pore spaces or when all of the latter are open and may be occupied with water. The former case is impossible, the latter is frequently realized with open-grained fire brick and similar materials.

In this investigation overburning was studied rather than normal conditions in order to bring out the readiness, varying for different clays, with which they become spongy, and to determine if possible how important a factor the inclosed pore space is in bringing about the swelling. At the same time it seemed desirable to follow the changes in density upon heating the clays beyond the stages of maximum strength and dense vitrification.

III. RESULTS

1. POROSITY DETERMINATIONS

In the following table the results of this work are compiled. Attention might be called at this point to the regularity with which the cones went down in the different burns, which is due to the fact that the same rate of firing was maintained throughout. This emphasizes the importance of associating the softening points of cones with definite rates of heating. It should become common practice to compare cone temperatures on the basis of time-temperature curves.

TABLE 1

Porosity Determinations on Specified Clays and Shales

CLAY NO. 1. CLEVELAND SURFACE CLAY

Temperature	Cone	Wet weight W	Dry weight D	Suspended weight	Approximate specific gravity	Average approximate specific gravity S_2	True specific gravity S_1	Approximate per cent porosity	Average approximate per cent porosity	Per cent true porosity due to sealed pores	Total per cent true porosity
°C											
1070	1	148.4	141.3	85.6	2.54	2.53	2.63	13.2	13.4	4.1	17.5
		144.2	137.2	83.0	2.53			13.5			
		143.3	136.3	82.4	2.53			13.5			
1090	2	138.0	132.9	80.6	2.54	2.53	2.61	10.0	9.2	3.1	12.3
		145.0	146.0	84.7	2.53			9.3			
		138.1	133.8	80.6	2.52			8.4			
1100	3	139.7	136.1	80.9	2.47	2.45	2.59	5.8	6.2	5.4	11.6
		140.6	137.6	81.2	2.44			5.7			
		142.3	139.0	82.4	2.46			6.1			
1130	5	149.4	139.7	78.0	2.26	2.31	2.57	17.7	19.3	10.7	30.0
		145.0	136.2	77.6	2.32			16.6			
		148.8	136.2	77.8	2.33			23.7			
1150	7	149.7	135.0	72.8	2.17	2.20	2.55	27.7	28.4	13.3	41.7
		149.8	135.3	73.0	2.17			27.0			
		152.3	135.9	75.5	2.25			30.7			
1170	8	153.8	136.9	77.6	2.31	2.28	2.55	31.4	29.8	12.4	42.2
		148.4	133.2	74.6	2.27			29.1			
		157.3	141.3	78.9	2.26			29.0			
1190	9	158.0	143.2	75.4	2.13	2.13	2.52	26.0	33.4	18.1	51.5
		152.2	134.0	71.0	2.13			34.3			
		160.3	138.1	73.3	2.13			40.0			
1210	10	167.0	140.2	75.6	2.17	2.18	2.51	48.0	50.6	14.7	65.3
		171.5	141.7	77.0	2.19			53.2			
1230	.....	123.4	110.4	59.4	2.16	2.14	2.49	30.0	31.6	15.3	46.9
		177.6	156.6	82.6	2.12			33.3			

TABLE 1—Continued

CLAY NO. 2. CURTICE SURFACE CLAY

Temperature	Cone	Wet weight W	Dry weight D	Suspended weight	Approximate specific gravity	Average approximate specific gravity S_2	True specific gravity S_1	Approximate per cent porosity	Average approximate per cent porosity	Percent true porosity due to sealed pores	Total percent true porosity
°C											
1030	03	114.1	113.8	66.5	2.41	2.41	2.61	0.7	0.7	8.2	8.9
		108.1	107.8	63.1	2.41			.6			
1050	02	113.1	113.0	63.8	2.29	2.27	2.57	.0	.0	15.0	15.0
		109.7	109.6	60.6	2.24			.0			
1070	1	119.8	119.8	52.7	1.79	1.81	2.52	.0	.0	41.0	41.0
		115.0	115.0	50.7	1.79			.0			
		117.2	117.2	54.3	1.86			.0			
1090	2	143.8	116.2	35.5	1.44	1.38	2.515	60.0	47.4	82.4	129.8
		126.2	110.0	28.0	1.34			37.0			
		135.5	114.8	31.5	1.38			45.4			
1100	3	155.8	115.8	37.8	1.48	1.48	2.51	87.0	83.5	71.3	154.8
		152.6	116.0	37.3	1.47			80.0			
		149.6	109.9	37.3	.....			.....			
1110	4	133.1	109.6	29.3	1.36	1.30	2.495	53.4	47.0	92.0	139.0
		127.4	108.5	24.1	1.30			43.6			
		127.0	108.3	20.4	1.23			44.0			
1130	6	163.4	106.3	53.8	2.02	2.02	2.49	134.0	136.0	23.4	159.4
		167.0	107.2	54.1	2.02			139.0			
		174.2	115.4	54.7	.....			.....			
1150	7	154.8	102.7	51.9	2.02	2.00	2.485	126.0	126.3	23.0	149.3
		140.7	94.0	46.8	2.00			123.0			
		165.6	108.8	54.3	2.00			130.0			
1170	8	138.2	95.2	49.6	2.09	2.10	2.485	112.2	112.0	18.4	130.4
		127.2	87.7	46.0	2.10			112.0			
		116.5	80.6	42.6	2.12			111.1			

TABLE 1—Continued

CLAY NO. 3. GALESBURG, ILL., SHALE

Temperature	Cone	Wet weight W	Dry weight D	Suspended weight	Approximate specific gravity	Average approximate specific gravity S_2	True specific gravity S_1	Approximate per cent porosity	Average approximate per cent porosity	Per cent true porosity due to sealed pores	Total per cent true porosity
°C											
1030	03	143.7	129.3	79.0	2.57	2.56	2.67	30.0	29.0	4.2	33.2
		139.2	126.1	76.7	2.56			28.0			
1050	02	140.4	131.4	78.7	2.50	2.50	2.655	18.2	19.3	6.2	25.5
		141.6	131.5	78.9	2.50			20.4			
1070	01, 1	132.4	125.6	76.9	2.57	2.57	2.635	14.3	14.1	2.5	16.6
		138.4	131.1	80.0	2.56			14.6			
		134.3	127.8	78.8	2.58			13.4			
1090	2, 3	128.2	127.5	73.6	2.36	2.40	2.625	1.5	1.7	9.2	10.9
		125.0	124.1	72.3	2.40			1.9			
		127.1	125.8	73.4	2.40			1.7			
1110	4	127.7	127.5	73.5	2.36	2.35	2.605	.4	.4	11.3	11.7
		128.9	128.8	74.0	2.35			.2			
		128.9	128.6	74.2	2.35			.6			
1130	5, 6	134.5	123.5	70.2	2.32	2.35	2.59	23.0	25.2	10.8	36.0
		137.1	125.2	71.9	2.34			24.6			
		148.1	133.6	77.5	2.38			28.1			
1150	7	150.9	129.0	75.9	2.43	2.41	2.555	43.3	43.6	6.0	49.6
		149.1	127.2	74.4	2.41			43.8			
		143.5	122.6	71.7	2.41			43.7			
1170	8	155.4	129.9	73.9	2.32	2.32	2.535	49.8	48.5	8.7	57.2
		151.8	127.2	72.7	2.33			49.1			
		150.2	126.9	71.8	2.30			46.6			
1190	9	152.5	124.5	69.8	2.28	2.32	2.53	56.9	59.2	8.1	67.3
		155.7	125.7	72.1	2.34			60.3			
		157.7	127.3	73.0	2.34			60.4			
1210	10	179.4	143.7	78.9	2.22	2.20	2.495	62.0	59.2	13.3	72.5
		131.9	106.5	57.9	2.20			60.0			
		108.7	88.9	47.0	2.12			55.5			

TABLE 1—Continued

CLAY NO. 4. CLEVELAND SHALE

Temperature	Cone	Wet weight W	Dry weight D	Suspended weight	Approximate specific gravity	Average approximate specific gravity S_1	True specific gravity S_2	Approximate per cent porosity	Average approximate per cent porosity	Percent true porosity due to sealed pores	Total percent true porosity
°C											
1030	03	131.7	130.4	78.4	2.51	2.51	2.65	3.2	3.3	5.7	9.0
		131.6	130.0	77.9	2.51			3.3			
1050	02	128.6	128.5	75.4	2.42	2.42	2.63	.0	.0	8.7	8.7
		135.2	135.1	79.3	2.42			.0			
1070	01, 1	134.8	134.2	75.4	2.28	2.28	2.595	1.1	1.4	14.1	15.5
		127.9	126.9	70.7	2.26			2.0			
		126.9	126.3	71.7	2.30			1.2			
1090	2, 3	149.4	138.7	70.8	2.04	2.05	2.57	20.0	21.5	24.0	45.5
		135.8	124.6	64.2	2.06			23.0			
1110	4	159.0	133.7	73.6	2.22	2.23	2.565	48.5	49.8	17.0	66.8
		133.6	111.3	62.1	2.26			51.3			
		157.0	131.6	73.1	2.20			49.5			
1130	5, 6	171.6	130.7	71.3	2.20	2.20	2.56	80.4	75.7	18.0	93.7
		168.7	131.3	72.0	2.21			73.3			
		176.7	137.3	74.0	2.17			73.5			
1150	7	194.5	136.9	72.8	2.13	2.13	2.55	107.2	108.1	20.0	128.1
		194.5	134.7	72.1	2.15			111.0			
		188.0	132.7	69.2	2.10			106.3			
1170	8	220.2	132.7	63.0	1.90	1.90	2.53	167.0	165.6	33.2	198.8
		210.8	127.2	61.3	1.92			166.2			
		179.6	109.1	49.6	1.83			163.6			
1190	9	252.3	132.5	52.6	1.66	1.66	2.50	226.4	223.0	51.7	274.7
		247.2	130.7	51.5	1.65			222.7			
		248.6	132.6	53.5	1.67			220.0			

TABLE 1—Continued

CLAY NO. 5. UNION FURNACE NO. 2 FIRE CLAY

Temperature	Cone	Wet weight W	Dry weight D	Suspended weight	Approximate specific gravity	Average approximate specific gravity S_2	True specific gravity S_1	Approximate per cent porosity	Average approximate per cent porosity	Per cent true porosity due to sealed pores	Total per cent true porosity
°C.											
		147.1	135.0	79.8	2.44			23.8			
1090	3	142.7	131.9	77.6	2.43	2.45	2.655	22.0	23.7	8.8	32.5
		146.7	133.9	79.8	2.47			25.4			
		142.4	132.3	78.9	2.47			20.0			
1110	4,5	148.8	140.3	81.6	2.40	2.42	2.62	16.0	17.3	9.3	26.6
		144.6	136.4	79.2	2.40			16.0			
		136.6	130.3	75.8	2.40			12.6			
1130	6	142.9	136.5	78.9	2.39	2.39	2.61	12.2	12.3	9.1	21.4
		142.0	136.0	78.5	2.37			12.0			
		134.2	127.5	75.3	2.44			14.0			
1150	7	139.8	133.1	79.0	2.46	2.45	2.60	13.0	13.3	5.6	18.9
		143.6	136.7	81.1	2.46			13.1			
		144.0	137.6	81.6	2.46			12.0			
1170	8	134.5	131.5	74.8	2.32	2.37	2.58	6.0	8.0	10.0	18.0
		142.2	139.1	79.5	2.34			6.0			
		133.7	130.9	74.0	2.30			6.0			
1190	9	129.7	127.7	71.2	2.26	2.27	2.57	4.0	4.6	14.0	18.6
		140.0	138.1	76.9	2.26			3.7			
		147.8	137.5	80.3	2.40			20.0			
1210	10	139.4	130.6	76.0	2.39	2.38	2.55	17.0	17.4	7.4	24.8
		139.0	131.2	75.4	2.35			15.3			
		143.1	130.3	75.6	2.38			24.8			
1230	11	149.4	134.7	78.3	2.38	2.38	2.53	27.6	26.1	7.0	33.1
		151.1	137.0	79.2	2.37			26.1			
		154.2	137.9	79.5	2.36			30.0			
1250	12	149.7	134.6	77.6	2.31	2.33	2.505	30.0	29.3	8.4	37.7
		145.1	130.5	75.2	2.31			28.1			

TABLE 1—Continued

CLAY NO. 4. KITTANNING NO. 2 FIRE CLAY

Temperature	Cone	Wet weight W	Dry weight D	Suspended weight	Approximate specific gravity	Average approximate specific gravity S_2	True specific gravity S_1	Approximate per cent porosity	Average approximate per cent porosity	Per cent true porosity due to sealed pores	Total per cent true porosity
°C.											
		159.0	149.6	90.3	2.52			16.4			
1090	3	145.5	137.1	82.4	2.51	2.51	2.62	16.2	16.2	4.4	20.6
		145.3	137.0	82.3	2.51			16.2			
		149.3	142.6	85.8	2.50			12.2			
1110	4.5	153.5	146.7	88.3	2.51	2.50	2.605	12.0	11.8	3.7	15.5
		148.9	142.8	85.6	2.50			11.1			
1130	6	142.2	136.6	81.8	2.49	2.48	2.58	10.6	9.6	4.0	13.6
		152.7	147.9	87.9	2.48			9.7			
		142.3	138.9	81.9	2.44			6.2			
1150	7	138.5	134.4	79.5	2.45	2.45	2.545	7.7	7.2	4.0	11.2
		154.3	149.8	88.7	2.45			7.6			
		145.2	143.3	83.4	2.39			3.3			
1170	8	143.5	141.7	82.2	2.38	2.39	2.525	3.2	3.4	5.2	8.6
		146.2	144.0	83.9	2.39			3.8			
		140.0	138.9	80.5	2.38			2.0			
1190	9	151.6	150.8	86.9	2.36	2.38	2.520	1.6	2.0	6.0	8.0
		146.0	144.7	83.9	2.38			2.2			
		142.2	141.6	81.4	2.35			1.0			
1210	10	145.1	144.4	83.0	2.36	2.35	2.510	1.2	1.1	6.4	7.5
		147.0	146.3	84.2	2.35			1.1			
		136.2	135.9	76.7	2.30			.5			
1230	11	144.8	144.4	82.1	2.31	2.31	2.495	.7	.5	7.3	7.8
		142.7	142.5	81.1	2.32			.4			
		147.6	146.8	81.0	2.23			1.4			
1250	12	144.3	143.4	79.5	2.24	2.24	2.480	1.5	1.7	11.1	12.8
		146.4	145.1	80.5	2.24			2.2			

In Figs. 1 to 6, inclusive, the results of the porosity determinations are shown graphically. In each figure the ordinates of the lower curve are the inclosed pore space; those of the upper curve are the total pore space; the difference between the two gives the open pore space.

No. 1. Cleveland Surface Clay (Fig. 1).—In considering results of this kind it is well to remember that the accidental factors entering into this question are quite prominent. The initial structure of the clay, the method of molding, the rate of heating, the character

of the kiln atmosphere, shorter or longer periods of overfiring, all influence the porosity conditions. In the present case we have minimum absorption (2.4 per cent) and minimum porosity at 1110°, followed by a rather sudden increase in porosity. The clay does not become densely vitrified at any temperature. Overburning begins within one cone of minimum absorption with decided development of vesicular structure. Facts as these clearly show the impossibility of using such clays for the manu-

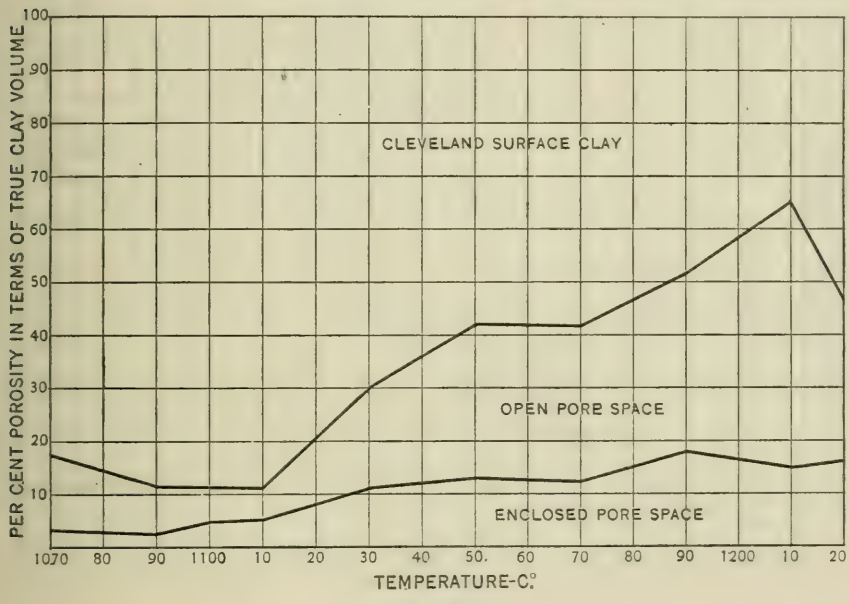

Fig. 1

facture of paving brick. The inclosed pore space also increased, though not so markedly as might be expected from the development of the porosity.

No. 2. Curtice Surface Clay (*Fig. 2*).—The conditions are very similar to those in the preceding case, with the exception that the vesicular structure develops very strongly and then subsides decidedly as the gases escape. In time, of course, still higher temperatures would cause more or less complete expulsion of the gases and reduction of total porosity, so that finally we should have a glass of no apparent porosity but still possessed of a system of inclosed pores.

No. 3. Galesburg Shale (*Fig. 3*).—This material reaches minimum absorption at between 1090° and 1110°, 0.5 per cent at 1090°, and zero at 1110°. At these points the open pore space is negligible in volume, but the vesicular structure has developed rapidly, beginning with 1070° C. For best results, therefore, the proper burning temperature should not exceed 1090°. The margin of safety of this material has clearly been shown to be small, as is

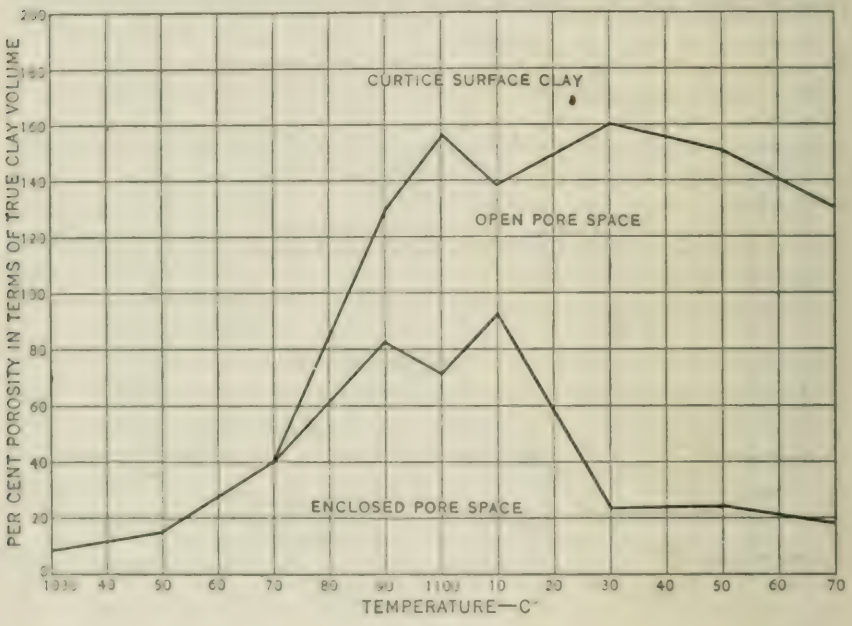

Fig. 2

typical of many Illinois shales. The importance of following the development of the vesicular structure is thus clearly indicated, since the ordinary porosity curve would fail to bring out the weakening influence of the factor in question. It is noted that the inclosed pore space diminishes again, though the total porosity is increased rapidly.

No. 4. Cleveland Shale (*Fig. 4*).—This material differs markedly from the preceding one inasmuch as the range of nonabsorption is very much longer. It is noted that the pore space represents practically altogether inclosed "bleb" structure up to 1070°.

From this point on the total porosity increases quite rapidly and the inclosed pore space more slowly.

No. 5. Union Furnace No. 2 Fire Clay (*Fig. 5*).—This clay shows a gradually decreasing total porosity with diminishing absorption,

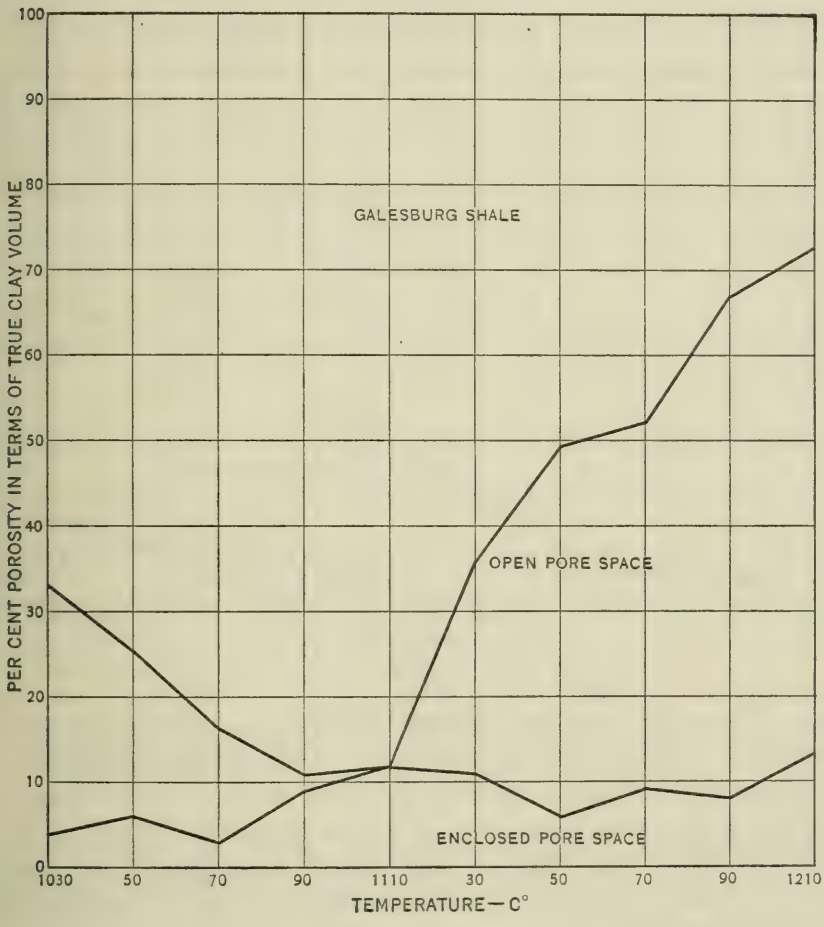

Fig. 3

interrupted between 1130° and 1170° by the increased vesicular structure. The lowest absorption is 2.14 per cent (in terms of the dry weight) and is reached at 1190°. From this point on the total porosity gains rapidly, although at the same time there is a

marked decrease in inclosed pore space. The diagram shows clearly that this clay can not be vitrified to a dense structure at commercial temperatures and hence would not be suitable for the manufacture of stoneware or similar products.

No. 6. Kittanning No. 2 Fire Clay (*Fig. 6*).—This material shows a markedly different behavior from the preceding clay of the same

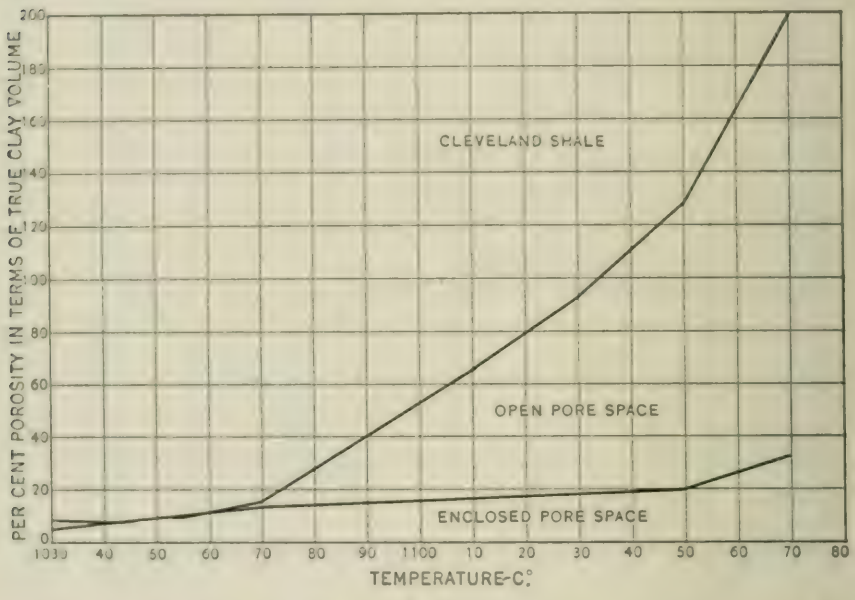

Fig. 4

type. Starting with an absorption of 6.28 per cent at 1090° it reaches practically complete nonabsorption, which condition is retained up to 1250°. At 1250° vesicular structure is developed, although the open pore space is not increased in volume. The diagram shows very strikingly the excellent qualities of this clay and its suitability for all products requiring dense structure and safe firing behavior.

2. SPECIFIC-GRAVITY DETERMINATIONS

The increase in the specific volume of these clays is shown by the tables, as well as by the curves of Fig. 7. It is at once observed that in no case a constant condition has been reached, but that the

density continues to decrease at a steady rate. This is further evidence tending to show that we are dealing here with a state far from equilibrium, which is reached only when complete fusion

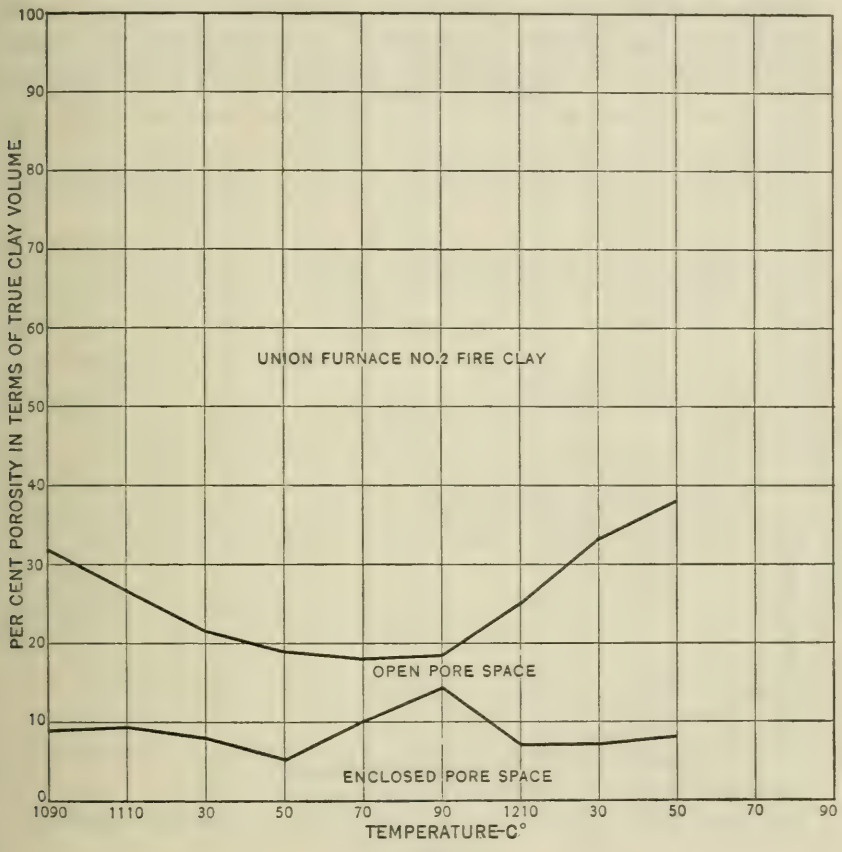

Fig. 5

has been brought about. It is interesting to note the drop on the specific gravities, which are as follows:

Clay	Maximum density	Minimum density	Difference
Cleveland surface clay	2.63	2.49	0.140
Curtice surface clay	2.61	2.485	.125
Galesburg shale	2.67	2.495	.175
Cleveland shale	2.65	2.500	.150
Union Furnace No. 2 fire clay	2.655	2.505	.150
Kittanning No. 2 fire clay	2.62	2.48	.140

IV. EFFECT OF THE CONDITIONS OF SHAPING

1. DESCRIPTION OF WORK

As has already been mentioned, the conditions of molding are of considerable importance, not only with reference to the initial porosity, but also in regard to the density developed at different

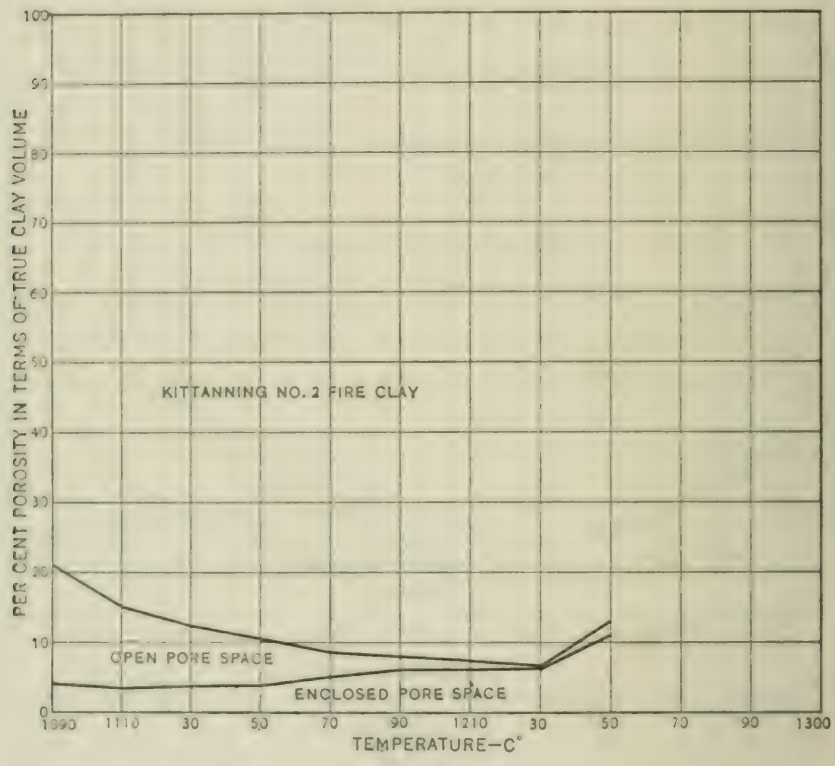

Fig. 6

temperatures. The comparison is especially interesting when the question of "overburning" is considered.

In order to illustrate the differences thus obtainable, the following experiment was made. A lot of Canton, Ohio, shale, well known for its safe vitrifying properties, was thoroughly mixed in the dry, ground state so that it truly represented a uniform sample. Part of this material was made up into brickettes in the plastic state; part was dry pressed in the moist condition, containing

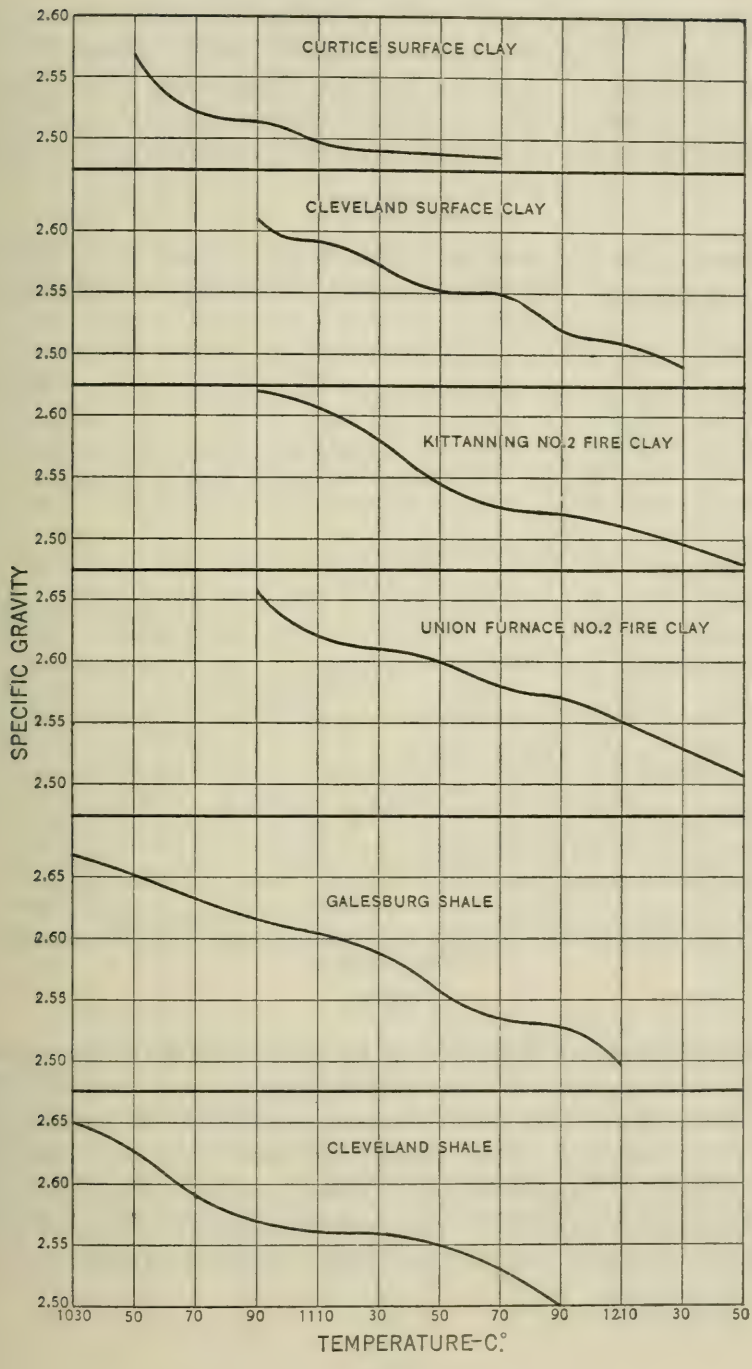
CURTICE SURFACE CLAY
CLEVELAND SURFACE CLAY
KITTANNING NO.2 FIRE CLAY
UNION FURNACE NO.2 FIRE CLAY
GALESBURG SHALE
CLEVELAND SHALE
SPECIFIC GRAVITY
2.60
2.55
2.50
2.65
1030
50
70
90
1110
30
50
70
90
1210
30
50
TEMPERATURE-C.°

Fig. 7

about 9 per cent of water. The specimens made from the plastic clay weighed about 80 grams when burned; the dry-pressed trials, about 40 grams. All of the dried brickettes were placed in the kiln close together and fired at the rate of 20° C per hour. After burning, the usual absorption and porosity weighings were made.

2. RESULTS

The results are shown graphically in the diagram of Fig. 8. As is to be expected, the initial porosity of the dry-pressed body is

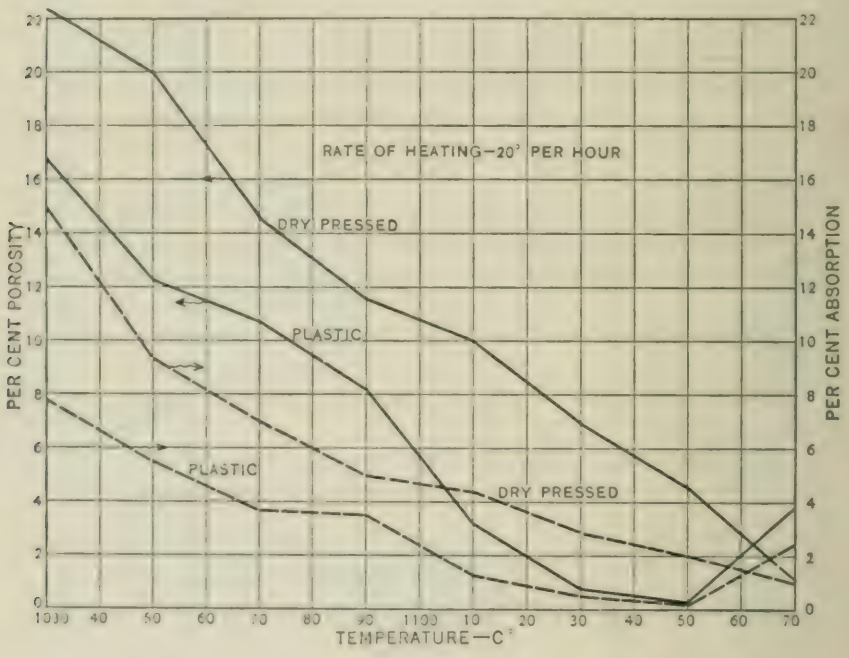

Fig. 8

considerably higher than that of the shale molded in the plastic state. Starting with 22.8 and 16.8 per cent porosity, respectively, the contraction of both kinds of specimens proceeds fairly uniformly and progressively down to about 3 per cent. At this point the contraction of the plastic body slows up. All along the two curves, however, points of equal porosity are separated by a considerable temperature interval, which becomes greater as the

3 per cent line is approached. Thus, a porosity of 6 per cent is reached by the plastic molded body at 1100°, by the dry-pressed body at 1138°. Similarly, 3 per cent porosity is obtained in the first case at 1111°; in the second at 1159°. Within the temperature limits employed the condition of nonabsorption is not reached at all by the dry-pressed body, while the plastic molded clay not only becomes impervious but even decidedly vesicular at 1170° C.

Here we have a case where the influence of physical factors is shown most prominently. The identical body presents an entirely different behavior according to whether it is made up in the plastic or the dry-pressed condition. At the same time, the well-known practical observation that dust-pressed clays require a higher maturing temperature is confirmed. If the two conditions of preparation were not known, the two curves would be considered to represent two clays of varying behavior.

V. SUMMARY

In the testing of clays the question of development of vesicular structure should receive careful attention and should be included in every complete report. Owing to the fact that the conditions of firing and other factors enter into the formation of inclosed pore space, carefully conducted burning is essential.

A definite rate of firing after the complete oxidation of the material should be maintained. The study of vesicular structure is more important in the case of materials where sound vitrification is required, as in the case of sewer pipe, paving brick, stoneware, electrical porcelain, etc., than for open-grained products. It is advisable to express all volume relations in terms of the true clay volume.

The continuous decrease in the specific gravity of the overburned clays shows that molecular changes are still going on and that equilibrium is by no means reached at the stages of complete and viscous vitrification.

Clays in the dust-pressed condition require a higher maturing temperature than when shaped in the plastic state and are less subject to the formation of vesicular structure.

WASHINGTON, May 15, 1913.

DEPARTMENT OF COMMERCE

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BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

No. 23

TECHNICAL CONTROL OF THE COLLOIDAL MATTER OF CLAYS

BY

H. E. ASHLEY, Associate Ceramic Chemist

Bureau of Standards

[NOVEMBER, 1911]

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1913

EDITORIAL NOTE

This paper, on Technical Control of the Colloidal Matter of Clays, was written by Mr. H. E. Ashley, but it had not been put into final shape suitable for publication. After the untimely death of Mr. Ashley, in 1910, Dr. John Johnston, of the Geophysical Laboratory of the Carnegie Institution, was asked to edit this paper. It seems advisable to state that Part I has been entirely rewritten, Part II has been rearranged and largely rewritten, while Part III is essentially as Mr. Ashley left it; but in all of this the editor has endeavored to correlate and elucidate the ideas expressed by Mr. Ashley in the original draft. Practically everything in this draft has been retained, for the editor did not, in the circumstances, feel justified in excluding any matter which might have a bearing on the subject in hand, and thus in some instances he has not been able to coordinate fully all the data obtained or cited by Mr. Ashley in the original draft. It might be stated that in order not to delay too long the publication of the results of Mr. Ashley's work it was decided not to take into account the recent literature since 1910.

THE TECHNICAL CONTROL OF THE COLLOIDAL MATTER OF CLAYS

By H. E. Ashley

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I. INTRODUCTION

The applicability of chemistry to the problems of clay working has been seriously limited in scope by the fact that the nature of clay products is dependent more on the physical properties of the raw materials than on their chemical composition. In other words, purely chemical knowledge does not help us here to the extent that it does, for instance, in the manufacture of iron and steel. In this industry the assured place of the chemist is due to the fact that the properties and behavior of the finished product are dependent above all on its chemical composition, and that the physical form in which the raw material reaches the plant is completely destroyed in the furnace, in which it is melted to a homogeneous fluid whose composition and properties may be exactly controlled. The clay worker, on the other hand, retains in his finished products, in large measure, the original physical structure of the raw materials. The grains of the crude kaolin or quartz form the actual skeleton of the finished ware, modified indeed, in the process of manufacture, but nevertheless possessing more or less complete physical identity.[1] The metallurgist establishes by fusion a new uniform basis of operations; the clay worker, with nice adjustment, utilizes the peculiarities of existing physical forms and perpetuates them. A definite chemical analysis tells the metallurgist what the capacities of his material are. Long and tedious experimentation, conscious planning, and more or less subconscious instinct enable the clay worker to adapt his material to the desired production.

[1] Zoellner: Sprechsaal, **41**, pp. 471, 490, 504, 519, 533; 1908; C. A., **2**, 3271. Mellor and Austin: Trans. Eng. Ceram. Soc., **6**, pp. 129–141; C. A., **2**, 3132; 1908.

In the clay-working industry the possibility and extent of replacing empirical by exact knowledge has been enormously increased by our greatly widened and improved knowledge of the nature and behavior of colloids; this has been gained, mainly in the last few years, as the result of a very large number of investigations, nearly all of which were made directly because of the enormous practical importance of colloids, especially, perhaps, in connection with the science of agriculture.

These researches indicated that many of the problems of clay working are very intimately connected with the nature and amount of the colloid matter in the clay. Consequently the first investigation begun by the clay-products section was upon the behavior of the colloid matter in clays; this occupied the year 1909.

Amongst the problems on which it was hoped that light would be thrown by such an investigation are: The control of the plasticity of clays, the control of the casting process for making clay wares, the securing of maximum density and strength in clay wares, the analytical separation of colloid and crystal matter in clays, the determination of the sizes of the grains of clay down to 0.01 mm, the prevention of excessive loss from the cracking of clay wares in drying, the prevention of white scum on brick, etc. A preliminary account of part of this work has already been the subject of a paper,[2] in the preface to which A. V. Bleininger writes:

> The most characteristic property of clays is their plasticity, on which depends their use in the arts. Yet this peculiar function of clay has been the most difficult to explain and to measure. Heretofore no criterion has been found which would enable the clay worker to compare with any degree of accuracy the varying degrees of plasticity found in the clays employed in industry. In this paper Mr. Ashley has made an attempt to explain the character of the plastic constituents of clay in the light of recent researches in the field of colloids, and also to offer a method for the comparison of the different clays with respect to this property. He is dealing, therefore, with a subject which is of fundamental importance not only to the scientific investigator but also to the manufacturer, for the success of the practical operations of shaping and drying hinges largely on the character and amount of the plastic matter present in clays.

In the present paper the questions treated in the bulletin just cited are discussed more fully on the basis of further experimental work and of a wider study of the literature pertaining to the subject in hand and to the chemistry of colloids.

---

[2] U. S. Geological Survey, Bull. 388, 1909. The Colloid Matter of Clay and its Measurement, by Harrison Everett Ashley.

1. THE ARGUMENT

In its briefest terms the argument pursued in this paper is: That the plasticity of a clay is directly determined by the character and amount of the colloid matter in the clay; consequently, by measuring and controlling the colloid matter present, we shall be able to control the plasticity of the clay and to obtain the great advantages incident to such control. The first statement above—that the plasticity of a clay is a function of the character and amount of the colloid matter present—is, we believe, generally accepted; we shall, however, bring forward additional evidence in support of it. To justify the second statement is the main aim of the present paper.

Before proceeding further it seemed advisable to give a short sketch of the present status of the chemistry of colloids in as far as it pertains to the subject in hand, and to define and discuss briefly certain of the physicochemical concepts which are introduced in the subsequent discussion. This has been included for the reason that some of the technical workers—to whom this paper is specially addressed—may not be familiar with the exact significance of the ideas and terms in question.[3]

Following this introduction and the brief exposition of some of the terms used there is a general discussion of the subject in hand supported by experimental work on clays, concluding with some applications of the work to specific problems. This order is, however, not rigidly adhered to. The references to the work of other investigators are not assembled in any particular portion of the paper. In some places they are inserted as confirmatory of results obtained; in others they are wholly depended on for essential information. As the literature of the subject is very voluminous, it has doubtless happened that credit has not always been given to the original investigator of some principle, though the effort has been made to do so.

[3] For fuller information, the reader is referred especially to Wolfgang Ostwald, Grundriss der Kolloidchemie (referred to hereafter as Wo. Ostwald, Kolloidchemie; a second edition of this book is now appearing) or to H. Freundlich, Kapillarchemie. These books represent the latest and most thorough treatment of the subject of colloid chemistry, and will be referred to in the text. Also Richard Zsigmondy, Colloids and the Ultra-Microscope, translated by Jerome Alexander, published by John Wiley & Sons, 1909 (referred to in the text as Zsigmondy, p. —). An excellent brief account is given by Viktor Pöschl, Einführung in die Kolloidchemie. The physicochemical concepts are treated of in practically all books on physical chemistry, of which James Walker's Introduction to Physical Chemistry (Macmillan's) may be recommended for clearness and accuracy of statement.

A. PRESENT-DAY VIEWS OF THE CHEMISTRY OF COLLOIDS[4]

From his classical experiments (1861–1864) on diffusion and dialysis (diffusion through a membrane, e. g., parchment paper, bladder, etc.) Graham was led to divide substances into two groups, according as the rate of diffusion is comparatively large or exceedingly small. Substances belonging to the latter group he termed "colloids," in contradistinction to the rapidly diffusing group of crystalloids, which, as its name implies, comprised for Graham substances which crystallize well from (and are therefore fairly soluble in) water; the chief examples of this class are salts generally and soluble organic substances (e. g., sugar) of comparatively simple structure. The colloids, on the other hand, were in general substances of very slight solubility in water, and in many cases of complex structure; the typical examples of this class are gelatin, gums, starch, etc.

On this theory then—the so-called chemical theory of colloids—the two classes of substances are chemically distinct; consequently substances belonging to one group should always exhibit the properties characteristic of that group. But there is now overwhelming evidence that this distinction does not hold—that typical crystalloids may under certain conditions behave as colloids, and conversely. For instance, sodium chloride has been obtained in colloidal form by von Veimarn,[5] while, on the other hand, it was found by Paterno[6] that tannin and gallic acid, which in aqueous solutions are typical colloids, give, when dissolved in glacial acetic acid, freezing-point depressions which correspond to normal molecular weights; consequently solutions of these substances in acetic acid are to be regarded as "true" solutions. Moreover, we are now in possession of ample evidence, obtained largely by means of the ultramicroscope, that there is a perfectly continuous progression as we pass from coarse visible suspensions through colloidal solutions to "true" solutions,[7] and one

[4] This section purports only to be a very brief sketch of that portion of the subject which is especially connected with the behavior of clays. This remark applies, mutatis mutandis, to all of the definitions and theoretical discussion presented in this paper.

[5] Z. Chem. Ind. Kolloide, 7, p. ..., C. A., 5, p. 621; 1911.

[6] Z. Physik. Chem., 4, p. ...; 1889.

[7] Cf. p. ..., postea.

substance may under proper conditions appear in any of these forms.

Therefore, it is now generally concluded that it is not advisable to distinguish between colloid and crystalloid substances; that the term "colloid" is not descriptive of an inherent property of a substance, but of its properties in relation to another substance. In other words, "the theories of colloid chemistry do not deal with colloidal substances, but with the colloidal state of substances." Similarly, "colloid phenomena are not, strictly speaking, the properties of colloidal substances, but are the peculiarities which are exhibited as a first approximation by a given substance, when it is observed in the colloidal state."[8]

This change of viewpoint has resulted in a change in nomenclature, so that it is now usual to speak of the "disperse phase" and the "dispersive medium," the former for the "colloid," the latter to designate the second constituent of the "colloidal solution." The newer terms are preferable because they imply nothing except the obvious fact that the colloidal state is not a strictly homogeneous state of matter;[9] in other words, in the colloidal state more than one phase [10] is present.

According to the newer views, the phenomena peculiar to the colloidal state are conditioned largely, or entirely, by factors due to the fineness of grain of the disperse phase and the consequent relative increase in extent of the aggregate surface of separation between the disperse phase and the dispersive medium. In general the surfaces of the individual particles of the disperse phase will be convex; that of the dispersive medium will be concave.

2. CLASSIFICATION OF DISPERSE SYSTEMS

Many schemes of classification have been proposed, all more or less arbitrary; the most useful are those in which the classification depends on the nature of the surface of separation of the two

[8] Wo. Ostwald, Kolloidchemie, p. 145.

[9] In the main part of this paper, however, the term "colloid matter of clay" is used throughout for the sake of convenience; but since in this special case the presence of water as the dispersive medium is always understood, this usage will lead to no confusion.

[10] A phase, in physicochemical usage, is defined as a mass chemically and physically homogeneous, or a mass of uniform concentration. (See Bancroft's The Phase Rule.)

components of the system. The most general scheme is that given by Wo. Ostwald,[11] as follows:

Dispersive medium	Disperse phase		
	Gaseous	Liquid	Solid
Gaseous	Class 9: G+G—No real example, as gases always are completely miscible	Class 8: G+L—Fog, e. g., at the point of liquefaction of gases, atmospheric fog, etc.	Class 7: G+S—Smoke, cooled ammonium chloride vapor, etc.
Liquid	Class 6: L+G—Foams	Class 5: L+L—Emulsions	Class 4: L+S—Suspensions; gels.
Solid	Class 3: S+G—Gas inclusions in minerals (e. g., pumice) or in metals	Class 2: S+L—Liquid inclusions in minerals; occluded water; water of crystallization	Class 1: S+S—Inclusions of solid particles in minerals; solid solutions

It is, of course, obvious that no hard and fast distinction can be drawn, for there is a continuous change of properties as we pass from one class to another. The above classification is given merely to show the generality of the phenomenon of dispersion and because such a scheme may aid us in applying the results and conclusions obtained with one class to any other.

3. EMULSION AND SUSPENSION COLLOIDS (EMULSOIDS AND SUSPENSOIDS)

These two groups make up what has been termed "colloid chemistry," and are by far the most important of all the groups. The properties of typical examples of each group show marked divergences, and accordingly they have been distinguished by various names. Thus, A. A. Noyes [12] calls them "colloidal solutions" and "colloidal suspensions," respectively; the former characterized as "viscous, gelatinizing, colloidal mixtures, not (easily) coagulated by salts," the latter as "nonviscous, nongelatinizing, but readily coagulable mixtures." They have also been termed "lyophile" and "lyophobe."

Practically the same distinction is made in the two terms "sol" and "gel," which, however, are often more loosely used. In this

[11] Kolloid-chemie, pp. [illegible]. This classification was also made independently and about the same time by E. E. Free (J. Phys. Chem. [illegible] 169, p. [illegible]; 1911).

[12] J. Am. Chem. Soc., 27, p. [illegible], 1905. For a fuller discussion, see Wo. Ostwald, Kolloidchemie, pp. 97 et seq.; Freundlich, Kapillarchemie, p. 309 et seq.

paper the word "sol" is used to denote colloid conditions similar to the typical gold sols or sols of other metals; gel to denote gelatinous or jellylike colloids.

No definite distinction can be made between these two; thus colloidal alumina and silica—constituents of the colloid matter of clays—may appear in either form or change from one form to another, according to the conditions. Moreover, there is no absolutely sharp line of demarcation between emulsoids and "true" solutions, on the one hand, and between suspensoids and coarse visible suspensions, on the other. This is equivalent to the statement that the properties of such disperse systems [13] vary continuously with the degree of fineness of the particles of the disperse phase, or with the aggregate extent of its surface per unit of weight; in other words, the properties vary with the degree of dispersion.

Of this there is ample proof. Perhaps the best illustration is some work of P. P. von Veimarn [14] on the form in which barium sulphate appears when it is precipitated by mixing equivalent solutions of barium thiocyanate and manganese sulphate in progressively increasing concentrations. These experiments showed that from the most dilute solutions were formed crystals of measurable size, which with increasing concentration diminished progressively through the microscopic to the ultramicroscopic; while from the concentrated solutions (about 0.1–10 *N*) colloidal sols and finally gels of gradually increasing permanence were obtained.

4. NATURE OF THE PARTICLES OF THE DISPERSE PHASE

On the basis of these observations von Veimarn has propounded the theory that matter always has the crystalline form, the size of the crystals varying from microscopic down to molecular size. He considers the molecules in the interior of the close-packed crystal to be very rigidly restricted as to freedom of motion, while those at the surface have a much greater degree of freedom, approaching that of the liquid state, and even capable of dissolving substances (adsorption). If, then, the crystals of a substance are

[13] Including "true" solutions as a limiting case.

[14] This work and the deductions von Veimarn has made from it form the basis of the numerous papers which he has published during the last few years in Z. Chem. Ind. Kolloide. It is more fully summarized by Johnston and Adams, J. Am. Chem. Soc., 33, pp. 837–839, 1911.

of smaller and smaller size, there will be a larger and larger proportion of incompletely oriented molecules until finally the substance as a whole possesses those properties that we call colloidal. These views are in harmony with a large number of diverse observations.[15] For instance, Mellor,[16] from mathematical considerations and from observations on melting behavior, concluded that the smaller the particles the lower the temperature at which the surface of the particle will begin to show signs of its diminishing viscosity; in other words, the smaller the particles the lower the observed softening temperature. Mayer [17] also practically demonstrated that feldspar in fine powder shows an earlier softening point than when coarse ground.

On the other hand, Freundlich concludes from a review of the matter,[18] "The suspensoids contain in general particles, whose diameter lies between $250\mu\mu$ [19] and $6\mu\mu$; sometimes also particles less than $6\mu\mu$ in diameter. The particles are probably approximately spherical and amorphous."

It seems inadvisable, therefore, in the present state of our knowledge to state that disperse particles are always crystalline, though in many cases they doubtless are. It may be well to observe here that "colloid" and "amorphous" should not be used as synonymous terms. Many substances, and amongst them the most familiar typical colloids, when dispersed in water, are apparently amorphous; yet this may easily be due to their vanishingly small real solubility in water, which would tend to cause the formation of masses of exceedingly small crystals. The probability of this is indicated by the following considerations.

In the course of the experiments quoted above von Weimarn has shown that the size of the particles of any specified precipitate diminishes progressively as we increase the degree of supersaturation of that precipitate with reference to the medium in which it is being formed. The degree of supersaturation is defined as the ratio of the total [20] concentration of substance to the concentra-

[15] See Wo. Ostwald, Kolloidchemie, pp. 115 et seq., 1917.

[16] Pottery Gazette, 45, pp. [illegible], 1920; Trans. Eng. Ceram. Soc., 9, p. 126, 1910.

[17] Jour. Am. Ceram. Soc., 4, p. [illegible], 1921.

[18] Kapillarchemie, pp. [illegible].

[19] μ = the one-millionth part of a millimeter. The above dimensions ($.25$ and $.006\mu$) represent the limits of the ultramicroscope. Particles larger than $.25\mu$ are visible in the ordinary microscope.

[20] That is, the aggregate weight of the substance as precipitate and remaining in solution divided by the total volume of the medium in which the reaction took place: cf. C. A., 5, p. 621.

tion of its saturated solution in the particular medium employed. The physical form of the products of a chemical reaction therefore depends wholly on the conditions under which it is carried on and can be varied at will from amorphous to coarsely crystalline. For gel formation the reaction must be as rapid as possible, therefore, by the interaction of concentrated solutions in solvents in which the reaction product is very sparingly soluble.

Conversely, even substances of such pronounced gelatinous character as aluminum hydroxide may be obtained in the crystalline condition if they are formed very slowly from dilute solutions. The number of centers of crystallization must be kept small, the total volume of the reacting solutions must be very great, a long time may be necessary, and a solvent must be used giving as large a solubility as possible. Crystallization is also promoted by means that artificially increase the solubility, namely, increase of temperature and pressure, introduction of foreign substances, etc. The principal and absolutely essential condition for the formation of stable fine suspensions is the exceedingly small solvent power of the medium for that particular material. Subsidiary conditions are that the velocity of formation of the substance whose suspension is desired must be considerable, and the concentrations of the reacting solutions must lie within definite limits. If these conditions can be fulfilled, a stable sol of any substance may be obtained. Moreover, since a very slight solubility is the most likely to be accompanied by a high degree of supersaturation, we should expect to get the finest particles with those substances which have the slightest solubility in the particular medium. In other words, substances which readily assume the colloidal state in water tend to be complex substances of high molecular weight—qualities which are usually associated with very slight solubility in water. Thus this serves to account for the old distinction between colloids and crystalloids.

On this view it should be possible to obtain any substance in the colloidal state if we can precipitate it rapidly in a medium in which it is very slightly soluble. The exact character of the disperse system thus produced will depend on the solubility and on the relative rapidity of precipitation. And this is in complete harmony with experience. Moreover, if we vary the medium in

such a way that the solubility of a given substance is decreased, but keep other conditions constant, we may change a sol into a gel. Therefore, if we add to a sol a reagent which by interaction with the disperse phase produces a phase less soluble in the particular medium than the original disperse phase, we shall by this means apparently coagulate the sol. What we have really done is to change the constitution of the disperse phase in such a way that the sol has been transformed into a gel. This is important, for, as we shall see later, this transformation is of very frequent occurrence with clays.

5. MECHANISM OF SUSPENSION

According to Stokes's formula the limiting velocity of fall v of a spherical particle of radius r through a fluid is given by the expression

$$v = \frac{2r^2g}{9k}\left(d - d^1\right)$$

where k is the viscosity of the fluid, d and d^1 the density of fluid and particle, respectively, and g the acceleration of gravity. From this it is evident that for a given fluid and for particles of given material the limiting rate depends directly on the size of the particle.[21]

It is evident, first, that for a finite size of particle the velocity of fall can never become zero. Theoretically, therefore, permanent suspension can not occur with particles the density of which differs from that of the surrounding medium. Practically, however, since the velocity of fall varies with the square of the radius, it is easily possible to find particles so small that their fall is almost infinitely slow, so slow in fact as to be entirely counteracted by convectional and other circulations which it is impossible entirely to eliminate from the medium itself. Practically permanent suspension is therefore possible by the action of well-known physical factors, even without the necessity of invoking those chemical combinations and electrical and molecular-kinetic actions which seem to come into play in the finer grained of the disperse systems.[22]

This view has received striking confirmation from recent work, especially by Perrin,[23] who, by counting the number of particles

[21] The particle is assumed to be spherical; deviations from spherical form would necessitate correction terms in the above formula, but do not invalidate the present argument. Incidentally, it may be observed that "true" solutions exhibit an entirely analagous behavior, for in a solution containing particles (ions) of different relative weights, the heavier particles tend to concentrate at the bottom of the solution under the action of gravity or, when the solution is centrifuged, away from the center of rotation. This has been definitely proved by R. C. Tolman (Proc. Am. Acad., **46**, pp. 109–146, 1910; C. A., **5**, p. 15, 1911).

[22] E. E. Free, J. Franklin Inst., **169**, p. 427, 1910.

[23] Perrin, Compt. rend., **147**, pp. 475, 530, **149**, pp. 477, 549; summarized by Perrin (Le Radium, **6**, p. 353, 1909, 7, p. 245, 1910, and in the newer books on colloid chemistry).

at different levels in thin films of certain suspensions, has calculated values of the Avogadro constant N (the number of molecules in 1 gram-mol), which are in excellent agreement with values of this same constant obtained by totally distinct methods.[24] In one of these N is calculated from measurements of the amplitude of the Brownian movement by means of a formula deduced by Einstein [25] from kinetic-theory considerations. This also serves to show that the kinetic theory is sufficient to account for the phenomenon of the suspension of fine particles. The characteristic darting motion, known as the Brownian movement, is shown by all suspensions containing particles less than 0.004 mm (4μ) in diameter; it is shown strongly by clay suspensions. Indeed, Atterberg [26] defines clay as particles under 0.002 mm diameter, which show Brownian movement strongly (0.003 mm show it only weakly).

W. H. Brewer [27] noted that "Those substances which retard the 'Brownian movements' hasten the 'precipitation' of fine-grained sand, flocculant clays, and pulverized charcoal when suspended in water." This, which has been confirmed by Duclaux,[28] is in harmony with the preceding statements.

The conclusions to be drawn from the foregoing discussion may be summed up: To say that a substance is in the colloid state (with reference to another substance, water in practically every case) is equivalent to the statement that the substance is dispersed throughout the water to form particles of which the diameter may range all the way from molecular up to microscopic and macroscopic dimensions. The size of the particles is determined by the method of formation of the disperse system (as it is now generally termed). The properties exhibited by the system vary with the fineness of the particles (the degree of dispersion); consequently the phenomena produced in disperse systems by variation of external conditions or by addition of reagents—apart from purely chemical effects, such as the ordinary solvent effect of hydrochloric acid upon colloidal ferric hydroxide—are due to variation in the degree of dispersion produced by the change of circumstances.

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[24] The most probable value of N from all the determinations is, according to Perrin, 68.5×10^{22}.
[25] Ann. Phys., **17**, p. 549, 1905; Zs. Elektrochem., **13**, p. 41; **14**, p. 235.
[26] Landw. Vers. Sta., **69**, p. 135, 1908.
[27] Mem. Nat. Acad. Sciences, **2**, p. 165, 1883.
[28] J. chim. phys., **5**, pp. 29–56, 1907; Z. Chem. Ind. Kolloide, **3**, p. 161, 1908.

6. PHENOMENA OF FLOCCULATION AND DEFLOCCULATION [29]

The process of coarsening or sedimentation of the particles is now commonly termed *flocculation;* the opposite process *deflocculation*. The latter term especially has come to mean a decrease in the rate of clearing, and suspensions are said to be *deflocculated* when they settle slowly or not at all. These terms are relative only, for we have no direct measure of the extent of flocculation. It is, however, convenient to speak of the *degree of flocculation*. Thus, when we say that addition of an alkali decreases the degree of flocculation, we understand that an alkali tends to deflocculate the system; or, in other words, to decrease the size of the disperse particles and so to render the suspension more permanent.

The degree of flocculation depends upon the surroundings of the system; but the influence of these external circumstances is by no means clearly made out, except that rise in temperature causes practically always an increase in the degree of flocculation. As compared with these external effects the addition of many material agents, sometimes in very small amount, has a great, and more thoroughly investigated, effect.

Indeed, this is the main way in which changes in flocculation are brought about in practice, and here lie the main technical applications of the phenomenon. Of the bodies which have large influences the main are the stronger alkalies and the organic colloids which decrease the degree of flocculation, and neutral salts and acids which increase it. The former are the "deflocculators," the latter the "flocculators." [30]

Turning first to the action of the flocculating agents—the acids and neutral salts—and considering the effect of varying concentrations of these bodies, the most noticeable fact is that a certain minimum concentration of the salt in the solution is necessary before there is any apparent action on the suspension. The absolute value of this initial active concentration (the so-called threshold concentration) varies with the different salts, but once attained the flocculating action on the suspension begins suddenly and continues rapidly * * *.

Next in importance to the effect of concentration is the effect of the chemical nature of the salt, and here we have two general rules. The first is due to Hardy [31] and states that a suspension (or colloid) will be flocculated only by a solution or another suspension whose ions or particles are of opposing electrical sign.[32] That is, a suspension the particles of which carry negative charges will be flocculated only by a solution containing positive ions, and vice versa. * * * The second rule is that of Schulze,[33] and says that the flocculating power of an ion increases very rapidly with its valence.[34]

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[29] For much of the contents of this section the writer (J. J.) is indebted to the admirable presentation given by E. E. Free: The Phenomena of Flocculation and Deflocculation (J. Franklin Inst., 169, pp. 421–438, 170, pp. 1–[illegible], 1910).

[30] Free, loc. cit., p. 427.

[31] Proc. Roy. Soc. London, 66, p. 115; 1899.

[32] Cf., p. 17.

[33] J. prakt. Chem. 2, 25, pp. 445–446; 1882.

[34] Free, loc. cit., pp. 430–431.

The deflocculators, which comprise only the hydroxides, carbonates, and other highly hydrolyzed salts of the alkali metals (all of which therefore have a strong alkaline reaction), also show the "threshold concentration" effect. Their behavior will be more fully discussed in their application to the specific case of clay.[35]

The flocculating action of acids and salts is probably the resultant of a number of factors, but there is little doubt that the most important primary factors are the effect of the salt or acid on the solubility relations and on the electric charges of the system.

For an understanding of the first of these it is necessary first to recognize that the separation between each suspended particle and the medium surrounding it is seldom a sharp one. The best instances are the emulsions. An emulsion of, say, chloroform and water really consists of a solution of chloroform in water in which are suspended droplets of a solution of water in chloroform. This mutual solubility of the two bodies probably has a great effect on the character of the surface of the particles, and since the nature of this surface is known to be active in controlling sedimentation and flocculation, it is to be expected that the amount of the mutual solubility will importantly influence the latter phenomena. But soluble bodies are likely to influence the solution equilibria of systems to which they are added, and it is therefore probable that their addition to emulsions will have noticeable effects on the mutual solubility of the particle and the medium, hence on the surface of the particle, and finally on the degree of flocculation. In the chloroform-water emulsion, above mentioned, the addition of a salt to the chloroform-in-water solution (the medium) will usually influence the solubility equilibrium between this and the water-in-chloroform solution (the particle); the quantities of water dissolved in the particles and of chloroform dissolved in the medium will change; and the surfaces of the particles, the degree of flocculation, and the other properties may change in turn. These relations are most obvious in the case of emulsions, but they apply, changed only in degree, to the solid-particle suspensions. * * *

The second way in which dissolved salts may act on suspensions is by changing the charges of electricity which are known to be resident on the surfaces of the particles. The action of these charges on flocculation might be either direct or indirect. In the first case the mechanism would be ordinary electrostatic repulsion. When the particles were all charged and of the same sign, there would be a repulsive force tending to prevent flocculation. The addition of salt solutions furnishes a means of changing the charges [36] on the particles, and hence of modifying this electrostatic resistance to flocculation. If the charges on the particles be reduced to zero, this resistance to flocculation will disappear, and flocculation may take place. There are, in fact, certain colloids and suspensions for which the point of zero electric charge (the "isoelectric point") corresponds to the greatest degree of flocculation. * * * These actions may be used to explain the rules of Hardy and Schulze, above mentioned. The action of suspensions of opposing charge in precipitating each other

[35] See p. 63 et seq.

[36] In terms of the most generally accepted theory of solution, this action is to be ascribed to the charges carried by the ions.

may obviously be ascribed to neutralization and the destruction of the electrostatic resistance to flocculation. The increase in the flocculating activity with increase of valence of the active ion is explainable on the supposition (already reached on electrochemical grounds) that the charge carried by an ion increases with its valence.[37] * * * Moreover, the sudden action at the "threshold" concentration (which shows practically no variation with increase of concentration thereafter) is exactly the course of events to be expected if the action is due mainly to the neutralization of electric charge, for this would be completed by the addition of a definite amount of the neutralizing material.[38]

With respect to secondary actions, definite knowledge is lacking. For instance, electric charges may produce indirect effects in opposing or assisting the surface tensions or other forms of energy resident on the surface of suspended particles; but the nature and action of these forms of energy is as yet very little understood.

It seems probable, therefore, that two of the ways in which dissolved bodies influence the phenomena of flocculation are by acting on the mutual solubility of the particle and the medium and by changing the electric potential at the surface of the two. Assuming that these actions can go on side by side and in varying degree, with the predominance now of one and now of the other, we have a reasonable explanation of the almost infinite complexity of the resultant actions which we actually observe. Add to this the known existence of still other factors of which we have as yet no understanding, and the existing confusion of knowledge does not seem surprising.[39]

These arguments and conclusions have been quoted at considerable length, because it seems to the writer that we can not hope to correlate the phenomena actually observed in the case of clays except with the aid of considerations analogous to those just advanced, and in addition of special ones which may seem to apply to the particular case, e. g., the effect of interchange of bases. (See p. 22.) And it is surely preferable to refer the observed effects to some phenomenon concerning which we have some positive knowledge rather than to some cause—for instance, to absorption, to which the reactions of clays have frequently been attributed—about which our knowledge is partly contradictory and largely uncertain. Yet it seems advisable to say a few words about absorption in general before passing on to the considera-

[37] In this connection it may be pointed out that it is possible that the Schulze rule may be accounted for in certain cases as follows: That this behavior is due to the smaller solubility of many salts of metals of higher valence as compared to that of the corresponding salts of metals of lower valence; and this in turn would tend to promote the metathetical reaction which occurs in certain cases on addition of a salt to a colloid, e. g., clay. (Cf., p. 74.)

[38] Free, loc. cit., pp. 414-415.

[39] Free, loc. cit., p. 436.

tion of the "absorption" by clays, which, as we believe, is due in large part to chemical reaction—a double decomposition—between the clay and the "absorbed" salt.

7. ABSORPTION

It is somewhat difficult to give a brief definition of the term "absorption" which shall be free from objection. Consequently we shall limit ourselves to stating that we use the term in its broadest sense, without theoretical implication. To take examples at random, the dyeing of fibers, the taking up by charcoal of gases and vapors, are cases of absorption.

Now, it is generally thought that absorption is a surface action, and hence purely physical in character; and so it doubtless is in many cases. But in other cases there is good evidence that a part is also played by purely chemical effects which sometimes may predominate to such an extent that the effect of the purely physical factors may be neglected entirely. For instance, the typical case of absorption by charcoal is generally referred to the physical surface effect, yet there are experimental data which indicate that purely chemical factors ought to be taken into account, at least in the absorption by charcoal of certain substances.

Thus, Glassner and Suida [40] found that benzine will extract from soot a substance which takes up dyes from aqueous solution. The soots, sugar charcoal, and wood charcoal contain hydrogen and oxygen; those which are the most active absorbents contain the most oxygen. Further, the same amount of one and the same charcoal always, under equal conditions, from concentrated or dilute solutions will take up very nearly the same amount of dye.

Knecht [41] has shown that the affinity of animal charcoal for acid dyestuffs like crystal scarlet varies with the percentage of nitrogen in the charcoal. Also that the affinity for basic dyes like methylene blue may be decreased by heating the charcoal with aluminum powder or zinc dust, and then treating successively with hydrochloric and hydrofluoric acids. The opinion expressed by Paterson and by Glassner and Suida that animal charcoal owes its decolorizing action to the presence of organic compounds

[40] Annalen, **361**, p. 353; 1908.
[41] E. Knecht: J. Soc. Chem. Ind., **27**, p. 949; **28**, p. 700; C. A., **4**, p. 1382, 1910.

stable at red heat is upheld by Knecht. He also discusses the decolorizing action of other forms of charcoal, such as coconut charcoal, lampblack, acetylene black, and naphthalene black, and shows that the more closely the substance approaches pure carbon in composition the less is its decolorizing property. He thinks it probable that absolutely pure amorphous carbon, however fine its state of division, would be found to be devoid of any decolorizing power on either acid or basic dyestuffs.

This behavior indicates chemical action, yet it must be recognized that the absorption by charcoal of such neutral and inert gases as argon, nitrogen, methane, ethylene, carbon monoxide, and carbon dioxide can hardly be attributed to chemical action. This question was investigated by Miss I. F. Homfray,[42] who came to the conclusion that the absorption of gases by charcoal can best be explained by the solution hypothesis, wherein the charcoal is considered as a strongly undercooled liquid (in the same sense that glasses are undercooled liquids). On the other hand, the work of Walker and Appleyard [43] on the distribution of a dye between water and silk indicates that the absorption of dyestuffs by silk is not a case of solution.

Hence absorption by charcoal, of certain substances at least, may be accounted for without the necessity of assuming the existence of surface films of extraordinary pressure and of remarkable solvent power. This, of course, by no means excludes the possibility that in many cases the purely physical effect is the predominating factor.

Incidentally it may be remarked that we can not deduce anything as to the mechanism of the process of absorption from the fact that the experimental results can be expressed by the so-called absorption equation or absorption isotherm. According to this equation

$$x/a = k\,c^{m}$$

where x is the absorbed amount, a the absorbing surface (usually measured by the weight of absorbent), c the initial concentration of the solution, and k and m constants, derived by calculation or by a graphical method from the experimental results themselves.

[42] Zs. Physik. Chem., **74**, pp. 129–201, 1910; C. A., **4**, p. 2896.
[43] J. Chem. Soc., **69**, p. 1334, 1896.

The reason that no conclusion as to mechanism can be drawn from agreement of experiment with the absorption equation is that, since no theoretical explanation is implicit in the derivation of the equation, it is possible by means of such an exponential equation with properly chosen constants to fit with fair accuracy any series of observations, provided only that the quantities in question change continuously in one direction only,[44] a condition which is fulfilled in a very large number of series of experimental results.

As stated above, there is evidence that absorption by charcoal may be a chemical reaction. When we study the "absorption" by minerals of salts in solution, there is a much greater weight of evidence in favor of the view that the phenomena in question are to be ascribed to an exchange of bases between the mineral and the salt.

This matter has been very fully treated by E. C. Sullivan,[45] who from a discussion of previous investigations and from his own experimental work concludes:

> The natural silicates precipitate the metals from solutions of salts, while at the same time the bases of the silicates are dissolved in quantities nearly equivalent to the precipitated metals. The bases most commonly replacing the metals in these processes are potassium, sodium, magnesium, and calcium. When exact equivalence is wanting, it is attributable either to solubility of the mineral in pure water or to the precipitation of basic salts. The metals are precipitated as hydroxides or basic salts with more or less silicate * * *. Adsorption, a mechanical surface action, plays a comparatively insignificant part, if any, in the retention of copper by kaolin. If adsorption is lacking in the case of kaolin, it seems reasonable to assume that it is lacking in the case of other silicates also.[46]

This makes it evident that in the case of clays, effects due to absorption will in general be unimportant as compared with those caused by the exchange of bases. Accordingly, this question will be considered somewhat more in detail, as it is important in connection with the reactions of clays.

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[44] This is equivalent to the statements (*1*) that the first derivative (the differential coefficient) shall not change sign; (*2*) that there shall be no maxima or minima in the curve.

[45] The Interaction between Minerals and Water Solutions, U. S. Geological Survey, Bull. 312, 1907, which contains copious references to the previous literature of the subject. Later references are: F. W. Clarke: U. S. Geol. Survey, Bull. **330**, p. 425, 1908. A. Reychler: J. Chim. Phys., **7**, pp. 362–368; C. A., **3**, p. 2644, 1909. F. Cornu: Min. pet. Mitt., **25**, pp. 453–455. E. Jordis: Z. Elektrochem., **13**, p. 525, 1907. E. Jordis: Z. Chem. Ind. Kolloide, **3**, pp. 22, 24, 1908. P. Ehrenberg: Landw. Jahrb., **38**, pp. 857–861, 1909; C. A., **4**, p. 1521, 1910. Fred W. Morse and Bert E. Curry: A Study of the Reactions between the Manurial Salts and Clays, Mucks, and Soils, 19th and 20th annual reports of the N. H. Agr. Exp. Sta., pp. 271–310, 1908. Hall and Gimmingham: J. Chem. Soc., **91**, p. 667, 1907. Hopkins: U. S. Dept. Agr., Bur. Chem., Bull., **78**, p. 14.

[46] Sullivan, loc. cit., p. 64.

8. EXCHANGE OF BASES

(*a*) EFFECT OF ACID OR NEUTRAL SALT SOLUTIONS UPON SILICATES

To quote again from Sullivan's discussion:

So far as the evidence goes, then, the action of silicates, clay, and other constituents of the earth's crust on solutions of such salts as do not dissolve in water with alkaline reaction consists in an equivalent exchange of bases. Any absorption of the salt as a whole by the solids mentioned is so small as to have escaped detection. As bearing on the latter point it should be said that certain colloid substances do take from solution both the acid and base of the salts mentioned. Ferric and aluminum oxides and metastannic and stannic acids, for instance, take potassium sulphate from solution, while hydrated manganese dioxide takes up sulphate, chloride, and nitrate of potassium. This of course does not necessarily imply absorption. It is not at all impossible, as van Bemmelen suggests, that chemical reaction takes place. Manganese dioxide takes up more base than acid from a neutral salt solution, and thus imparts to the solution acid reaction. Cupric oxide takes more of the acid and alkalinity results. These and other similar reactions suggest the reaction between mercuric oxide and potassium chloride, where potassium hydroxide forms owing to the slight electrolytic dissociation of mercuric chloride, and they may be due to similar causes. The solids capable of absorbing both acid and base from a neutral salt solution are in the main those which themselves exercise both basic and acidic functions.[47]

Now, the metallic salts, the aqueous solutions of which are neutral or acid, comprise for practical purposes the salts of the strong acids—the chlorides, nitrates, and sulphates; hence, the reaction consists in an interchange of bases between the silicate and salt, resulting in the formation of a slightly different (insoluble) silicate and of a soluble salt.[48, 49]

(*b*) EFFECT OF ALKALINE SOLUTIONS UPON SILICATES

Alkaline solutions comprise, in addition to the solutions of the free alkalies, solutions of those salts which are formed by the union of a strong base with a weak acid, and consequently undergo hydrolysis. Now the weak acids commonly met with—for instance, carbonates, phosphates, sulphides (also silicates themselves)—are precisely those acids which form slightly soluble salts with the bases most commonly present in silicates, e. g., calcium, iron, magnesium. Therefore, with alkaline solutions the final

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[47] Sullivan, loc. cit., pp. 13–15.

[48] If silicates containing barium or strontium were brought in contact with sulphate solutions, probably only an appreciable quantity of the difficultly soluble sulphate would be formed on account of the very slight solubility of the silicates of these metals, a solubility which is probably much less than that of their sulphates. Of course some calcium would be formed, the amount of which could be calculated from the principle of mass action if the solubilities of the sulphates and silicates were known.

[49] An exception to this statement is afforded by such acid solutions as the solution of calcium carbonate in water containing carbon dioxide; the reason for this is obvious.

effect is slightly more complex than with acid solutions, for in addition we have the following two reactions:[50]

1. The free alkali may react with free (colloidal) silica, thus forming a substitution product. This serves to account for the fact that the absorption of free alkali (potassium hydroxide) by clay is greater after the clay has been extracted by acid, a process which removes some of the bases from the clay and is therefore analogous to, or indeed identical with, exchange of bases. It may be remarked that in general free alkali has a greater action on silicates than a neutral salt has. The reason of this was pointed out by Rümpler,[51] namely, that when potassium hydroxide acts on a silicate the calcium and magnesium which are removed are at once precipitated as hydroxides and therefore do not tend to put a stop to further substitution of potassium by promoting the reverse reaction, as their soluble salts would do.

2. The metal displaced from the silicate combines with the acid in the solution to form a slightly soluble salt, which accordingly is precipitated from solution. This accounts for the "absorption" by soils and clays of a soluble carbonate or phosphate; in reality more or less complete double decomposition takes place with the formation of slightly soluble substances only. The soundness of this explanation is confirmed by some early work of van Bemmelen,[52] who showed that extraction with hydrochloric acid, which dissolved oxides of iron and aluminum and decomposed silicates to such an extent that absorption and substitution would not take place, also did away with precipitation of the carbonate, phosphate, and borate radicals by the soil. Moreover, a soil thus extracted took up half the alkali from sodium carbonate solution, leaving the acid radical in its entirety as bicarbonate. To this it might be objected that extraction with hydrochloric acid destroys the absorbent power by removing the main absorbents—the (colloidal) iron and aluminum hydroxides. But to the writer the explanation given is more convincing; it is based on well-known facts and is in harmony with the observations; further it accounts quantitatively for the phenomena in some cases and would doubtless do so always if the solubility relations involved were accurately known.

[50] Whether, and to what extent, they take place, is determined entirely by the solubility of the possible product, or products, relative to that of the substances initially present.

[51] Report International Congress Applied Chemistry, 3, p. 59, 1903.

[52] Landw. Vers. Stat., 23, p. 267; 1879.

B. IMPORTANCE OF SOLUBILITY RELATIONS IN DETERMINING THE COURSE OF A REACTION IN SOLUTION

The importance of the fact that solubility, or perhaps we should rather say lack of solubility, is the predominating factor in determining the products of reaction of any system is not thoroughly appreciated by a very large number of chemists. The appearance of any one product is very often ascribed to the existence of a greater affinity between its component parts than exists between the components of the other compounds which might conceivably be formed by the reaction. In a certain sense this is true, but in the sense in which the term "affinity" is ordinarily employed it is fallacious and misleading. For example, consider the following reactions:

$$2AgNO_3 + BaCl_2 = 2AgCl + Ba(NO_3)_2$$
$$Ba(NO_3)_2 + Ag_2SO_4 = BaSO_4 + 2AgNO_3$$

From the first of these we should, according to the above reasoning, conclude that silver was a stronger base than barium, while from the second we reach the directly opposite conclusion.

As another example, take the statement, which appears in the majority of textbooks on organic chemistry, that tetramethylammonium hydroxide ($N(CH_3)_4OH$) can not be displaced from aqueous solutions of its salts (e. g., the chloride) by potassium hydroxide, because the former is the stronger base. But it has been shown that if we choose a medium (methyl alcohol) in which one of the products (potassium chloride) of the reaction is insoluble, the reaction

$$N(CH_3)_4Cl + KOH = N(CH_3)_4OH + KCl$$

takes place and yields practically the theoretical amount of the tetramethylammonium hydroxide.[53]

These two examples,[54] which are typical of a very large number of similar cases, demonstrate that the relative strength of the competing acids and bases is a negligible factor in determining

[53] Walker and Johnston, J. Chem. Soc., 87, p. 901, 1905.

[54] Another good example is this. If we add hydrochloric acid to a solution of sodium silicate, sodium chloride will be formed and silicic acid liberated, but yet at a very high temperature, as in the process of glazing earthenware, silicic anhydride in presence of water vapor is capable of decomposing sodium chloride with expulsion of hydrochloric acid. This behavior is not at first sight dependent on solubility relations, but it is perfectly analogous if we consider that volatility may be looked upon as solubility in a vacuum.

the product which separates out following a reaction in aqueous (or other) solution; the important factor is the relative solubility of the original substances and of the possible products of reaction. This behavior is in thorough accordance with the law of mass action and with the currently accepted theory of solution; so that if we know the solubility relations of all possible products (including complex salts, e. g., the double cyanides and oxalates, if such are formed), we can predict quantitatively the course of the reaction.[55]

Since a proper appreciation of mutual solubility relations and their consequences is important for the thorough understanding of the main part of this paper, an outline of the theory involved has been given. In this outline it has not been possible to enter into the practical limitations of this theory; these limitations are, however, generally of minor importance, and are absolutely unimportant here. Their effect is such that a lack of concordance of a few per cent may be found between theory and experiment.[56]

9. LAW OF MASS ACTION

Consider the reversible chemical action

$$A + B = C + D$$

where the letters represent single molecules of the substances, as in ordinary chemical formulæ. Then, according to the law of mass action, the state of equilibrium of the above system is determined by the equation

$$\frac{[A]\,[B]}{[C]\,[D]} = K$$

where the symbols [A], [B], etc., represent the "active masses" of the respective substances when equilibrium has been attained; K is a constant, the value of which depends solely on the external conditions (e. g., temperature). When the reaction takes place in a wholly gaseous system, the "active mass" of each substance is proportional to its molecular concentration; when the system is

[55] This statement is subject to slight limitations, which, however, are not of importance in the present connection, and hence are not discussed here. Compare footnote 56.

[56] The reader desirous of fuller information is referred to recent publications from the laboratory of A. A. Noyes, especially the papers of which W. C. Bray is sole or joint author. (Published in J. Am. Chem. Soc. during the last few years.)

an aqueous solution, the active mass of each reacting molecular species (which are, according to the current views, ions or undissociated molecules) is given by the concentration of that particular species (expressed always in molecular or equivalent concentrations).

As an example, take the reaction

$$KI + I_2 = KI_3$$

Writing the equation for the ions, we obtain

$$K^+ + I' + I_2 = K^+ + I'_3$$

or, eliminating what is common to both members of the equation, $I' + I_2 = I'_3$. Consequently it is the actual concentrations of these three molecular species which determine the equilibrium. The concentration of KI or KI_3 has no effect on the equilibrium, except through its relation to the concentration of I' or I'_3, a relation which in its turn is determined by exactly analogous equations, which determine the amount of ionization of each salt.

As an example of this, let us consider the dissociation of a weak acid (acetic acid). The dissociation equation is $CH_3COOH = CH_3COO' + H^+$. Applying the law of mass action we obtain the expression [57]

$$\frac{[CH_3COO'][H]}{[CH_3COOH]} = K$$

which is the well-known Ostwald dilution law,[58] as applied to solutions of acetic acid. This law is in agreement with the experimental observations on the so-called weak electrolytes, which comprise substances (mainly organic acids and bases) which are ionized less than 10 or 15 per cent; when applied to the class of strong electrolytes, substances which are ionized 60 per cent or more (all salts, strong acids, and bases), it apparently does not hold, but this discrepancy is without doubt to be attributed to the fact that hitherto it has not been found possible to obtain sufficiently accurate values of the *actual ion concentrations* when the *total* ion concentration is large.

[57] Throughout this paper symbols inclosed in brackets (e. g., [A]) denote the concentration of that particular molecular species.

[58] This is usually written slightly differently. Thus, if 1 mole of acetic acid is in solution in v liters of water, and if α is the fractional ionization, the concentrations of CH_3COO', H^+, and CH_3COOH are, respectively, α/v, α/v, and $(1-\alpha)/v$, and the expression becomes

$$\frac{\alpha^2}{(1-\alpha)v} = K$$

10. SOLUBILITY PRODUCT

Let us now examine the nature of the equilibrium between the aqueous solution of a salt and the solid salt itself. To each temperature there corresponds a certain solubility of the salt, i. e., a certain concentration of salt which is in equilibrium with the solid. Now, the salt in solution is present as unionized molecules and as ions; but all the evidence indicates that it is the concentration of the unionized portion which directly determines the equilibrium. The unionized salt here plays the part of intermediary between the solid and the ions; it is in equilibrium with the unionized solid on the one hand and with the ions on the other. Therefore, under constant external conditions, the concentration of the unionized portion will always be constant so long as an excess of solid salt is present.

Consider, now, a system made up of a saturated solution of the salt BA, together with excess of the solid salt, the external conditions remaining constant. On applying the law of mass action, as before, we obtain the relation

$$\frac{[B][A]}{[BA]}=K$$

Now, from what has just been said, [BA] is constant; therefore B] [A] = constant.[59] This is what is known as the constant solubility product.

11. EFFECT OF A COMMON ION IN DIMINISHING SOLUBILITY

If now we add an extra quantity of the ion B^+ (for instance, by addition of the soluble salt BCl), the concentration of A′ must diminish that the solubility product may remain constant. A′ can only fall out of solution along with an equivalent quantity of positive ion; and, since B^+ is the only kind of positive ion in the solution, a certain quantity of the salt BA must be precipitated in order to reestablish equilibrium.[60] Exactly

[59] This, too, is subject to certain limitations, unimportant here, which can not be discussed here. (Cf. footnotes 55, 56.)

[60] A numerical example may make this clearer. The concentration of a solution saturated with respect to silver bromate at 24.5° is 0.0081 *N*. If we assume the salt to be entirely ionized (an assumption which is very nearly true in a salt solution of such a feeble concentration), the constant solubility product is $[Ag^+][BrO'_3]=0.0081\times0.0081=0.0000656$. Now a quantity of silver nitrate is added, which when dissolved in the same water as contains the silver bromate would of itself make the solution 0.0085 *N* with respect to Ag^+ (this would correspond to about 0.01 *N* with respect to the total $AgNO_3$). Suppose that the concentration of silver bromate now remaining in the solution is x, a smaller quantity than before; $[Ag^+]$ is now, therefore, $(0.0085+x)$; $[BrO'_3]$ is x and $(0.0085+x)x=0.0000656$, whence $x=0.0049$. That is, the concentration of silver bromate in a 0.01 *N* solution of silver nitrate saturated with respect to silver bromate is 0.0049 *N*, as compared with 0.0081 *N*, the concentration of its saturated solution in pure water.

analogous reasoning holds for the addition of A′ (e. g., as the soluble salt KA). In other words, the solubility of a substance is lowered by the addition of a second substance yielding an ion common to both.

As common instances of the application of this principle, which is constantly made use of in practical work, the following may be cited: In purifying sodium chloride by recrystallization it is usual to precipitate the salt from a strong brine by the addition of concentrated hydrochloric acid. Sodium sulphide is used to precipitate the more soluble metallic sulphides, while hydrogen sulphide (in solutions of which the concentration of S″ is very small indeed) suffices to precipitate the less soluble sulphides.

The best known application of this principle, and the one which has given a name to the process, is the salting out of soap. When a fat has been saponified with moderately dilute caustic soda, the resulting solution contains glycerin and excess of alkali in addition to the soap, which consists of the comparatively slightly soluble sodium salts of some of the higher fatty acids. Thus the addition of a soluble salt like sodium chloride throws these salts almost completely out of solution as a curdy mass. If the fat has been saponified by a strong solution of caustic soda, the concentration of sodium ion may be great enough to throw the soap out as it is produced.

This is the process known as salting out, which now is used as a convenient term to designate the effect of addition of a common ion in diminishing the solubility of a substance. Incidentally it may be noted that this process of decreasing the solubility by driving back the extent of ionization is merely the limiting case of the commonly used process of driving back the dissociation of a (weak) base or acid (and hence reducing the "strength" of the base or acid) by adding a salt of the base or acid; thus in ordinary analytical work, ammonium chloride is added with ammonia, sodium acetate is added with acetic acid, in order to accomplish this object. One limitation to the general applicability of the process of salting out deserves mention, namely, that if complex ions are formed, the solubility of a substance may be increased, instead of decreased, by the addition of a common ion. Thus, silver cyanide is more soluble in solutions of potassium cyanide

than it is in water; this behavior is due to the formation of the complex ion $Ag(CN)_2'$ by the reaction $(CN)' + AgCN = Ag(CN)'_2$. This reaction, however, is also subject to the law of mass action; application of which yields the equation

$$\frac{[CN'][AgCN]}{[Ag(CN)_2']} = K$$

where K, the so-called complex constant, is exactly analogous to the solubility product of a simple salt.

Application to a specific equilibrium.—As a specific example of the application of these principles to the determination of equilibrium conditions, we shall consider the reversible reaction

$$BaSO_4 + Na_2CO_3 = BaCO_3 + Na_2SO_4$$

Here both the barium salts are insoluble. For the sake of simplicity we shall assume that the constant conditions are such that the concentration of neither of the sodium salts reaches the saturation point. The reaction may then be written

$$BaSO_4 + CO_3'' = BaCO_3 + SO_4''$$

There are present in the system the following molecular species: Un-ionized $BaSO_4$ and $BaCO_3$, Ba^{++}, SO_4'', CO_3'' [and Na^+ which, however, may be left out of account, since it plays no direct part in the reaction].

We have then the equilibrium equations between these quantities

$$[Ba^{++}][SO_4''] = k_1 \text{ and } [Ba^{++}][CO_3''] = k_2$$

where k_1 and k_2 are the solubility products of $BaSO_4$ and $BaCO_3$, respectively; and therefore, since Ba^{++} is common to both

$$\frac{[SO_4'']}{[CO_3'']} = \frac{k_1}{k_2} = K$$

In words, the ratio of the concentrations of sulphate ion and carbonate ion is constant. Therefore, if, after equilibrium has been attained, we add SO_4'' (as Na_2SO_4), $BaCO_3$ is transformed into $BaSO_4$, until this ratio reattains its constant value; conversely, the addition of CO_3'' causes the formation of $BaCO_3$ at the expense of the $BaSO_4$. In each case the amount transformed is perfectly definite; and the state of equilibrium can always be calculated if

k_1, k_2 and the concentration of either SO_4'' or CO_3'' is known. If the conditions were such that the system should become saturated with respect to sodium sulphate or carbonate (or both), the equation determining the equilibrium would be somewhat more complicated; but the general result would be the same, namely, that the position of equilibrium is determined by the relative solubilities (in the particular medium) of such of the possible products of reaction (which include the original substances) as separate out as solid phases.

C. NEUTRALITY OF AQUEOUS SOLUTIONS

According to the theory of electrolytic dissociation, acidity is attributed to the presence of hydrogen ion (H^+) and alkalinity to the presence of hydroxyl ion (OH') in the solution. Now, it has been found experimentally that the dissociation of pure water, according to the scheme $H_2O \rightleftarrows H^+ + OH'$, is such that $[H^+][OH'] = 1.2 \times 10^{-14}$ at 25°. Now, according to the above scheme, the concentrations of H^+ and OH' in pure water must be equal; each must therefore be

$$= 1.1 \times 10^{-7}$$

The condition of neutrality, therefore, is that $[H^+] = [OH']$, which is equivalent to the statement that either should be equal to 1.1×10^{-7} (at 25°); solutions in which the concentration of H^+ is greater than this are acid, those in which it is less (or the concentration of OH' greater) than this are alkaline. Thus, in a 0.125 *N* solution of hydrochloric acid the concentration of H^+ would be about 0.1 *N* (since such a solution is ionized to about 80 per cent); the concentration of OH' in such a solution would, therefore, be about 1×10^{-13}; for it is understood that the product $[H^+] \times [OH']$ must attain the constant value 1.2×10^{-14} in any aqueous solution, provided that the temperature is 25°.

Now, a good indicator changes color at a definite concentration of H^+; and the concentration of H^+ can be measured directly; a series of indicator solutions may, therefore, be prepared, such that each shows its characteristic color change at a hydrogen ion concentration ten times that characteristic of the solution preceding it in the series.[61] Such a series of indicators may then be used to

[61] Directions for the preparation of such a series have been given by Salm (Zs. Physik. Chem., **63**, p. 83 (1908)); the subject has been further discussed in a number of more recent papers.

establish the hydrogen ion concentration of unknown solutions, though when it is used for this purpose care must be taken to exclude possible reactions between the indicator and the components of the unknown solutions; otherwise the results may be of doubtful accuracy.

12. SALT HYDROLYSIS

It is a matter of common knowledge that the aqueous solutions of many salts are not neutral. Thus, for instance, sodium carbonate, sulphide, and silicate are alkaline; the chlorides, nitrates, and sulphates of most polyvalent bases are acid. This behavior is attributed to a process termed "salt-hydrolysis," which may be represented by the reaction $BA + H_2O \rightleftarrows BOH + HA$ and occurs (to an appreciable extent) only when the acid or the base (or both[62]), are weak.[63]

It is impossible to enter here into the theory of hydrolysis or to derive from the law of mass action the relations which determine its extent. Suffice it to say that under constant external conditions the extent of hydrolysis is perfectly definite and depends upon the magnitude of the dissociation constant of the weak acid [64] or the weak base;[65] or rather it is determined by the relation between this dissociation constant and that of water, so that the process of hydrolysis may be regarded as a competition for the strong base (or acid) between the weak acid (or base) and water (which may exercise either basic or acidic functions). Thus, in decinormal solution at ordinary temperatures, sodium chloride is practically not hydrolyzed, sodium acetate is hydrolyzed to an extent which is just appreciable (0.01 per cent), while sodium sulphide is hydrolyzed to somewhere about 90 per cent. With rise of temperature the dissociation constant of water increases faster than that of the acids and bases. Consequently the extent of hydrolysis increases markedly with rise in temperature. At all temperatures the extent of hydrolysis increases with diminishing concentration of the salt (except when both acid and base are weak).

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[62] This case is of less practical importance, hence its consideration is omitted here.

[63] The strength of an acid (or base), in the sense in which it is used here, is measured by its extent of ionization. Thus, in decinormal solution at 25° hydrochloric acid is ionized to about 85 per cent; acetic acid to about 1 per cent; hydrogen sulphide to about 0.1 per cent; corresponding to this the respective dissociation constants of these acids are 1 (approximately), 1.8×10^{-5} and 9×10^{-8}. The dissociation constant of water is, as given above, 1.2×10^{-14}.

[64] In salts which yield an alkaline solution.

[65] In salts which yield an acid solution.

It is important to observe that in determining the degree of hydrolysis we must employ a method which will not disturb the hydrolytic equilibrium. Thus, an attempt to measure the hydrolysis of a salt yielding an acid solution by titrating the free acid would fail for the reason that as fast as the free acid is neutralized more is formed by the process of hydrolysis, and the solution will not become neutral until all the acid which was originally combined with the weak base has passed into combination with the strong base with which the solution was titrated.

Conversely, the extent of hydrolysis can be diminished by the addition of hydroxyl ions (to alkaline solutions) or of hydrogen ions (to acid solutions). An understanding of this process is important, as it accounts quantitatively for the increased solubility in acid (or base) of certain salts, as follows: If a salt is made up of a strong acid and a weak base only slightly soluble in water, its solubility will be limited by the solubility of the free base formed by hydrolysis, although the unhydrolyzed salt is itself soluble. Consequently increasing the concentration of free acid by driving back the hydrolysis increases the amount of the salt which will stay in solution; this increase continues until the hydrolysis has practically disappeared, after which further increased concentration of acid is without effect on the solubility of the salt. The same explanation holds for the increased solubility, with increase of alkali concentration, of a salt containing a weak, slightly soluble acid. As examples of this we have the increased solubility of salts of iron or aluminum in solutions containing excess of free acid and of sodium silicate or aluminosilicate in solutions containing free base in excess.

II. THE CHEMICAL REACTIONS OF THE COLLOID MATTER OF CLAYS

In this section the principles outlined in the preceding section will be applied in an endeavor to correlate and elucidate the behavior of clays under varying conditions. The experimental observations adduced are in part taken from the voluminous literature pertaining to clays; in part they are the result of original work by the author (H. E. Ashley).

1. DEFINITION OF CLAYS

Clays may be defined as mixtures of minerals of which the representative members are hydrous silicates of aluminum, iron, the alkalies, and the alkaline earths, of which the most characteristic is the hydrated aluminum silicate ($Al_2O_3,2SiO_2,2H_2O$).[66] Some quartz, mica,[67] and feldspar are usually present; the grains of these minerals may show crystal faces (especially in the case of china clays), but commonly they are of irregular shapes.

Upon most of the grains of the constituent minerals there is an enveloping coating of colloidal material, which consists of silicates, silicic acid with hydroxides of aluminum,[68] iron, and manganese, and usually contains some organic matter.[69]

Almost any mineral, as well as various soluble salts, may be present in clays and modify the properties somewhat. The combination of granular and colloidal material is, or should be, in such proportion that when reduced to proper size (by crushing, sifting, washing, or other means) and moistened with an appropriate amount of water plasticity is developed. If too much colloidal material is present, the clay is considered very sticky, strong, or fat; if too little, the clay is called sandy, weak, lean, or nonplastic.[70] The term "nonplastics" for granular materials requires qualification, since most plastic bodies would lose plasticity and become sticky if the granular constituent were removed. The highly colloidal clays are as nonplastic as the clays containing little colloidal material. In one case the clay is too sticky to work; in the other case it is too weak and sandy. Plasticity depends on

[66] Mellor and Holdcroft (Pottery Gazette, **36**, pp. 680–686; 1911) present evidence in favor of the view that this is to be considered as a member of a series of complex aluminosilicic acids, which are no more closely related to the silicic acids than, for instance, the ferrocyanides are to the cyanides.

[67] Vogt (Contributions a l'Etude des Argiles et de la Ceramique, published by the Société d'Encouragement pour l'Industrie Nationale, 1906, pp. 193–218, 275–357) has most conclusively proved that muscovite mica ($3Al_2O_3,K_2O,6SiO_2,2H_2O$) is a frequent and considerable constituent of the "clay substance" of many of the clays of France, and often is the predominating constituent in Chinese and Japanese porcelain. It is as plastic as kaolin in a state of exceedingly fine division. (Cf., p. 39, and see also Bourry: Treatise on Ceramic Industries, translated by Rix, pp. 53, 702; 1901.)

[68] It is not at all unlikely that these may be present largely as aluminosilicic or ferrosilicic acids. (Cf., Mellor and Holdcroft, loc. cit.)

[69] For instance, Böttcher (Sprechsaal, **42**, pp. 233, 252; 1908) extracted from fire clay by ether about 0.1 per cent of a yellow waxy material, which had the odor of clay, was soluble in ligroin, benzene, and alcohol, but in water only slightly and with decomposition. It began to flow about 80°, burnt readily without residue, smelling like paraffin. Clay extracted alternately with water and ether settled much more quickly than before, had lost its fatty feel, and had a crystalline sheen.

[70] Cf., p. 38.

a proper ratio between colloidal and granular matter, but within limits it varies with the amount of colloidal material present. According to Schloesing [71] the proportion of colloidal material in a clay is usually small and rarely exceeds 1.5 per cent; a clay containing 0.5 per cent is lean.

It may be noted that it has been shown that the hydroxides of both aluminum and iron possess amphoteric properties [72]; that is, they can behave either as acid or as a base, depending upon the conditions. This is in accordance with certain observations of Hundeshagen,[73] who found that kaolin absorbs basic dyes very strongly, but acid dyes only very weakly, and concluded from this that kaolin may act not only as a weak acid, but also under other conditions as a very weak base. This possible amphoteric character of clays increases their capacity for reacting, but at the same time renders it more difficult to account for or to predict their behavior under all circumstances.

2. ORIGIN OF CLAYS

Clays have been formed by the decomposition of feldspars, though the exact mode of formation is not yet established beyond question. Thus Clarke writes: [74] "That kaolinite (the crystalline mineral of the composition Al_2O_3, $2SiO_2$, $2H_2O$) is the chief residual product of feldspathic decay is the commonly accepted view, but some writers hold that it is not formed by ordinary weathering. According to H. Rösler [75] kaolinite is only produced by pneumatolytic action—that is, by the operation of thermal waters and gaseous emanations. * * * Probably different crystalline silicates yield different residues of this ill-defined class (of hydrous silicates of aluminum and iron), and any or all of them may exist in residuary clays."

Whatever be the exact process by which feldspars are transformed into clays, this much is certain, that the main agency in the removal of the alkalies and silica is water (or dilute aqueous solutions). This removal may be effected by simple solution, for

[71] Chimie agricole, in Fremy's Encyclopédie Chimique, p. 67, 1888.
[72] J. K. Wood, J. Chem. Soc., 93, p. 411.
[73] Z. angew. Chem., 21, p. 2455, 1908.
[74] Data of Geochemistry, U. S. Geol. Survey, Bull. 330, p. 416, 1908.
[75] Neues Jahrbuch f. Mineralogie, etc., Beil. Bd., 15, p. 231; 1902.

we know that in the lapse of time water dissolves the constituents of alkaline silicate out of feldspar; the process is probably furthered by mechanical factors.

The complete disintegration of a rock is commonly followed by a removal of the fragmentary material from its original site. This transportation may be effected in various ways—by flowing streams, by glacial ice, or by winds—and it is accompanied to a certain extent by a separation of the rock residues into substances of different kinds. A stream deposits its load first as coarse gravel, then as sand, and finally, often with extreme slowness, as silt or clay. The gravel consists merely of fragments, more or less rounded, of the original rock or of its larger inclusions. The sand contains finer particles of undecomposed minerals, with quartz usually predominating. The silt is composed largely of decomposition products, such as kaolinite, hydroxides of iron or aluminum, and the like. These substances shade into one another, and their exact nature in any specific case will depend upon the thoroughness with which the primary decomposition was effected and upon mechanical factors such as the velocity of the stream.[76]

3. CHARACTER OF THE CLAY SUBSTANCE

As stated above, the characteristic constituent of clays is a hydrous aluminum silicate, the composition of which, as determined by analysis, is given by the formula Al_2O_3, $2SiO_2$, $2H_2O$; as yet, however, the constitution of these substances has not been definitely ascertained.

Löwenstein [77] concluded from weak evidence that the combined water of kaolin is given off in two stages, and therefore that it is not all of the same nature. This view has been shared by several investigators, including Le Chatelier. On the other hand, it was shown by Barnes [78] and confirmed conclusively by Kennedy,[79] and later by Mellor and Holdcroft [80] that the dehydration all takes place in one stage. The main conclusions reached by the last-named authors follow:

There is no definite temperatures above which it can be said that kaolinite [81] decomposes and below which kaolinite does not decompose. The speed of decomposition is accelerated by raising the temperature or by working under reduced pressure. The heating curve of kaolinite shows that an endothermal reaction occurs in the

[76] Clarke, loc. cit., p. 426.

[77] Zs. anorg. Chem., **63**, pp. 69–139; 1909.

[78] Clayworker, **23**, p. 705; 1895.

[79] Trans. Am. Cer. Soc., **4**, pp. 149, 152; 1902.

[80] The Chemical Constitution of the Kaolinite Molecule, Pottery Gazette, **36**, pp. 680–686; 1911.

[81] The authors here use the term "kaolinite" for a sample of china clay containing both kaolinite and "clayite"; the latter term has been adopted previously by Mellor (Pottery Gazette, **34**, p. 927; 1909) to denote "the noncrystalline variety of the hydrated aluminum silicate (Al_2O_3, $2SiO_2$, $2H_2O$) which occurs in china clay and in most clays yet examined. Kaolinite is crystalline clayite."

vicinity of 500°, and an exothermal reaction just over 800°; the former corresponds with a decomposition of kaolinite into free silica, free alumina, and water. The restoration of from 3 to 4 per cent of water, by heating calcined kaolinite [82] under pressure in steam, corresponds with a rehydration of alumina or silica. The formation of sillimanite (Al_2O_3, SiO_2) in kaolinite when heated over 1200° is due to the recombination of the free alumina with some of the silica formed at about 500°. The exothermal change shown in the heating curve of kaolinite corresponds with a physical change of the free alumina whereby the alumina becomes less soluble in acids, less hygroscopic, and more dense. Kaolinite may be represented as one member of a series of aluminodisilicic acids, and these in turn form one group of a large number of aluminosilicates.

Now, it is quite possible that the aluminosilicic acids are much stronger than the silicic acids, just as hydroferrocyanic acid is stronger than hydrocyanic acid; hence kaolinite, if it is an aluminosilicate, might not be hydrolyzed by water. If it were hydrolyzed, colloidal silica and alumina would be formed. The nature of this process is indicated by the following considerations:

It is well known that the solubility in water of any substance is never absolutely zero, although it may be exceedingly small. Consequently kaolinite in contact with water dissolves to some slight extent and is immediately hydrolyzed.[83] The solution thereby becomes unsaturated with respect to kaolinite; consequently more dissolves, which in turn is hydrolyzed, when still more can be dissolved, and so on. These two simultaneous processes may thus transform an appreciable amount of kaolinite, provided that sufficient time be allowed—a condition which would usually obtain. Whether a definite state of equilibrium is reached can not be stated at present with absolute certainty; it is probable, however, that equilibrium would finally be reached, though the position of equilibrium would likely vary—e. g., with the size of the colloidal (disperse) particles produced, consequently with the rate of the process, which in turn depends largely on the temperature. The products of such hydrolysis are of course alumina and silica, in general in the colloidal state, the degree of dispersion depending upon various factors; in some cases the water might contain salts in quantity sufficient to coagulate them wholly or in part.

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[82] It may be noted that kaolinite heated to higher temperatures is less sensitive chemically than when dehydrated at lower temperatures, and that the rehydrated material is not plastic. (Cf., p. 38.)

[83] This statement is, of course, subject to the condition that the acid is weak, a condition which holds presumably for silicic acid itself, although, as stated above, it may not hold for the complex aluminosilicic acids.

This point of view is in harmony with conclusions reached by H. Gedroiz,[84] who asserted that aluminum hydroxide, ferric hydroxide, silicic acid, and kaolin are at the moment of their formation by weathering hydrosols, which stay as such or are coagulated, depending on the composition of the soil solution.

It is not pretended that the mode of action outlined above has been effective in all cases; it is given merely as a simple view of the matter, by means of which differences in the gross composition of clays and in the character and amount of their colloid content may be accounted for.

In the lapse of time a renewed crystallization of the colloidal material may be set in. Thus, K. Endell [85] has analyzed and determined the colloid content of clays formed under fuel deposits of different ages, as follows: (1) Weathered basalt from beneath 0.30 m peat contained 60 per cent (by volume) colloidal material; (2) decomposed basalt from beneath 1.50 m peat, 87 per cent; (3) decomposed basalt from under brown coal, 67 per cent; (4) decomposed melaphyre from under bituminous coal, 50 per cent. He concludes that:

> Basic eruptive rocks are in general decomposed to kaolin [86] by overlying peat and its fossil relations, brown coal and bituminous coal. In the course of this decomposition there is an increase in the content of silica, titanium, aluminum, and water and a decrease in the phosphate, iron, alkaline earths, and alkalies, all of which are dissolved out more or less. * * * A comparative consideration of the proportion of colloidal material * * * shows first a gradual increase in colloids, which reaches its maximum with basalt decomposed under peat, then a gradual decrease, which may be attributed to renewed recrystallization of the newly formed colloids in the course of geological periods.

A. GENERAL PROPERTIES OF CLAYS

4. GAUGING THE COLLOID MATTER OF CLAYS

Clays exhibit their characteristic properties only in presence of water; indeed, that water is present is implicit in the definition of clay, for the behavior of the dried-out clay substance differs largely from that which we ordinarily associate with clays. Formerly a variety of ad hoc hypotheses were proposed to account for the properties of clay; but now, since the development of our knowledge of the colloidal state, all of these properties may be correlated with the presence in the clay of colloidal matter.

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[84] J. Exp. Landw., 9, pp. 272–293, 1908; C. A., 3, p. 2600, 1909.
[85] Sprechsaal, 43, pp. 278, 291, 1910.
[86] By "kaolin" Endell apparently means "clay substance" of formula approximating to that of kaolinite.

The principal properties of clay, besides its absorptive power, which we shall consider later, are *plasticity*, *binding power*, and *shrinkage* on drying or burning.

It is now generally believed that the plasticity of a clay is due to the colloidal substance which it happens to contain. This supposition was clearly stated by T. Schlösing [87] as long ago as 1888, and advocated later by P. Rohland.[88] It has recently been developed more fully by A. S. Cushman,[89] whose experiments upon the binding power of road-making materials are apparently conclusive.[90]

It is unnecessary to marshal here all the evidence in favor of this view; the following example may serve to illustrate how on this view one well-known phase of the behavior of clays may be simply accounted for. When clays have been completely dried, plasticity disappears (and with it the other characteristic properties); when the material is again wetted the plasticity is initially not so great as it was before drying out, but in the lapse of time increases slowly again. This behavior is exactly analogous to that which has been often observed with colloidal systems [91]; that is, the drying-out process in some way changes the state of the solid phase so that the degree of dispersion is less on wetting again than it was originally, and only regains its former value by means of the slow taking up of water, accompanied possibly by some degree of hydrolysis.

On this supposition, too, the other properties can be simply accounted for. Thus, to quote Rohland: [92]

On this hypothesis we may easily account for the phenomena of shrinkage on drying in the air and on burning, especially the fact that the shrinkage ceases before the mass is fully dry. Such a mass is to be regarded as a complex solid meshwork, in the pores of which a liquid phase is present. In this way the shrinkage of the solid network may cease, while liquid is still present in the pores.

The ability of a clay to take up and to hold relatively large amounts of foreign material (such as sand, powdered minerals, etc.) without destroying its other properties is also to be attributed

[87] Chimie agricole, in Fremy's Encyclopedie Chimique, p. 67.

[88] Z. anorg. chem., 31, p. 1[illegible], 1902; 41, p. 1[illegible], 1904; 56, p. 46, 1907; 60, p. 306, 1908; 65, p. 108, 1909; Z. Chem. Ind. Kolloide, 4, p. 5, 1909; J. Soc. Chem. Ind., 29, p. 12, 1910; 30, p. 23, 1911; 33, p. 5, 1910.

[89] U. S. Dept. of Agriculture, Bureau of Chemistry, Bulls. No. 82, 1904 and 92, 1905; Trans. Am. Ceramic Soc., 6, 1904. Cushman cites several other authorities than those mentioned above.

[90] Clarke, Data of Geochemistry, pp. [illegible].

[91] For instance, see Lottermoser and Rothe, Z. physik. Chem., 62, p. 175, 1908, who studied the deflocculation of colloidal silver particles and found that they could not be deflocculated once they had been completely dried or precipitated.

[92] van Bemmelen Gedenkboek, p. 28. (Published at Helder, 1910.)

to the presence of colloidal material, which surrounds the foreign particles, and thus binds them together.

Plasticity is exhibited not only by hydrated silicate of aluminum, the usual main constituent of clays, but also apparently by any silicate of a slightly soluble base (e. g., oxide of iron or zinc, magnesia) under conditions comparable to those where ordinary clay develops plastic properties. For example, Rohland states that a clay carrying zinc showed great plasticity,[93] and Le Chatelier [94] reports that a plastic paste may be obtained by grinding mica or glauconite with water for a sufficiently long time.

The shrinkage on burning is closely related to the plasticity, being greater as the plasticity is greater. This is in accord with the ideas stated above, for on drying there is a contraction around each individual grain due to the destruction of the colloidal material as such and the consequent formation of a multitude of cracks. It is practically impossible to dry a mass of pure clay so that it shall be free from cracks. But by suitable admixture of sand or other nonplastic material with the clay these cracks may be rendered small and separated one from another so that they do not endanger the strength of the ware. In order to accomplish this it is essential that the drying process be uniform throughout the mass. To insure uniformity the drying must be conducted very slowly, and more slowly in proportion as the material used was more plastic.

The shrinkage must not be too much reduced by the addition of foreign material; otherwise the hardness of the ware will suffer. Pure clay becomes very hard on drying, while sandy pastes always remain more or less friable. This correlation does not obtain if the burning is performed at a temperature such that a partial fusion of the material may occur; but it does hold for bricks, tiles, and other refractory materials, which are burned at temperatures between 1000° and 1200°.

From the foregoing we see the great practical importance of a knowledge of the amount of plasticity of clay bodies and of the

[93] van Bemmelen Gedenkboek, p. 29. Its analysis was: Loss on ignition 7.85 per cent; ZnO, 54.06 per cent; Al_2O_3, 1.64 per cent; SiO_2, 35.39 per cent; Na_2O, 1.80 per cent.

[94] van Bemmelen Gedenkboek, p. 167. Le Chatelier, however, attributes plasticity to the presence of exceedingly small crystalline lamellæ, and is of the opinion that all substances made up of such lamellæ will show plastic properties.

effect of added substances upon the plasticity. This is equivalent to a knowledge of the amount and character of the colloidal material and its behavior to reagents. This behavior we shall now consider in detail, describing first an easily applied test, previously described by the writer,[95] by which the comparative plasticities of clays may be gauged.[95a]

(*a*) MALACHITE GREEN TEST FOR GAUGING THE COLLOID MATTER OF CLAY

Procedure.—In brief and with slight modifications suggested by later experience the procedure is as follows:

Into a 100 cc cylinder provided with glass or rubber stopper put 50 cc of water. Add 1 gram (or other more suitable proportion) of clay, ground or sieved to the degree of fineness technically used, or to pass 60 mesh. Shake at once by hand to prevent clotting. Add 50 cc malachite green solution (6 g malachite green oxalate per liter). Shake gently for two hours on a mechanical shaker and allow to settle overnight. (It might be preferable to use a centrifugal machine.)

On the following day take out a convenient amount of the supernatant liquid by a pipette, the tip of which is inserted to the 60 cc mark on the cylinder, and run it into one of a pair of 50 cc comparison tubes, such as is used for carbon determinations in steel analysis. Into the other tube put 0.5 cc of the standard dye solution (6 g per liter, as above) and dilute to about 35 cc, the maximum concentration at which a good comparison can be made. Compare the tints in a camera with white glass plate (Eimer and Amend Catalogue No. 3821). Now dilute whichever tube is the darker until the tubes match. If either tube is not large enough for full dilution, make it up to 50 cc, take out 5 cc in a pipette, clean the tube with water, and return the 5 cc contents of the pipette to the tube. To insure uniform mixture

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[95] H. E. Ashley: The Colloid Matter of Clay and its Measurement, U. S. Geol. Survey, Bull. 388, 1909; Trans. Am. Cer. Soc., 11, pp. 417-475, 1909.

[95a] EDITORIAL NOTE.—While the malachite green test may yield a fairly good comparative measure of the plasticity of clays, it can hardly be accepted as a measure of the colloid content; for the absorption of a dye by colloidal material depends upon the character (degree of dispersion) as well as upon the amount and composition of the latter. Notwithstanding this, the test may prove of decided service with similar clays or with series of samples of the same clay. See, however, a paper by H. Stremme and B. Aarnio (Zs. prakt. Geol., 19, pp. 129-133, 1911), who have shown that malachite green is affected by the presence of lime or alkalies; they conclude that the Rodewald-Mitscherlich hygroscopicity determination is the most satisfactory method of gauging the colloid content of clays.

on diluting, empty the tube twice into a 100 cc beaker after each addition. If the dye stains the glassware, it may be removed easily by a little acetic acid.

Keep results in the following form:

Kind of clay	Weight taken	cc of dye solution added	Color comparison				Grams dye remaining in solution		Grams dye absorbed	
			Standard		Test					
			cc taken	Diluted to—	cc taken	Diluted to—	Per cc	Total	Total	Per 1 g clay
Boone....	1	50	0.5	420	10 1	10.4 1.04	0.000 007 43	0.000 743	0.299 257	0.299 257

The number of grams dye in 1 cc of the test solution is then $\frac{1.04 \times 0.003}{420} = 0.000\ 007\ 43$; the total dye remaining in solution is therefore 0.000 007 43 × cc liquid taken (100) = 0.000 743, and the total amount of dye absorbed = 0.3 − 0.000 743 = 0.299 257.

This does not give the colloidal matter directly, but by comparison with the absorption found under similar conditions with a very plastic clay as standard (for which purpose the writer has used Tennessee No. 3 Ball of the Tennessee Ball & Sagger Clay Co.) the relative plasticity may be gauged. For example, if the clay tested shows a total dye absorption 1.25 times as great as that of the standard (taken as 100) its relative plasticity is 125.

The absorption of malachite green is in all probability an exchange of bases such as is discussed later in this paper. The dye is a salt of a complex ammonia base which forms insoluble compounds with the colloidal acid radicals, while its oxalate radical forms insoluble oxalates with the bases which tend to keep clay coagulated. Therefore its reaction with the colloidal matter is very complete. It fails, indeed (is decolorized), with alkaline and limy clays, which, however, are not included among the clays used for the better classes of clay wares. As both the sulphate and chloride of this dye are soluble in water, no serious interference can be ascribed to such soluble salts as occur in clays. No other dye is so free from objections and so well suited for colloid measurements. (Cf. Table X, pp. 72–74.)

(*b*) SODIUM CARBONATE TEST

According to Bleininger:[98]

Plasticity is sometimes measured by letting 1 g of clay stand in a solution of normal sodium carbonate, then determining the amount absorbed by the decrease in the strength of solution. The amount of sodium carbonate absorbed is supposed to be proportional to the colloids, which colloids are supposed to be the seat and source of plasticity.

According to the views advanced in this paper, the sodium carbonate precipitates those bases which are combined with gels but is unaffected by those with the sol. The method seems sound, except that an excess of alkali appears to act on the crystal matter if sufficient time is allowed. (Cf. time effect, p. 44; casting, p. 98.)

(*c*) WATER STORAGE

The more abundant colloidal matter is in a clay the more water it can store in an "air-dry" condition. This is illustrated by the following determinations of the loss of weight of air-dried clay: (1) When heated at 60° in a slow current of air that had been dried by bubbling through strong sulphuric acid; (2) when heated further to 130°.

The table of relative colloid content shows that the amount of water absorbed by clays from the air at ordinary temperature and humidity and given up again to dry air at 60° or 130° is very nearly proportional to the colloid content. As humus matter is the most absorbent colloid in soils, it follows that humus is of value in dry weather as a water reservoir.

	Loss from "air-dry" condition to—		Relative colloid content by malachite green oxalate test
	60° C	130° C (total)	
	Percent	Per cent	
Texas, Edwards County, white fire clay	3.08	3.78	154
Potters' Supply Co., Tennessee ball No. 3	1.60	2.11	100
J. Poole, No. 20 English ball	1.35	1.77	98
Jas. P. Prall, New Jersey No. 1 sagger	1.28	1.61	100
P. L. Ryan, New Jersey No. 1 sagger	1.24	1.54	78
Moore & Munger, English ball	1.22	1.46	91
Edgar Bros.' Co., Florida kaolin	0.91	1.13	33
Johnson Porter Clay Co., Tennessee X wad	0.45	0.53	22
J. Poole, No. 1 china clay	0.30	0.44	24
Potter's "flint" (quartz)	0.05	0.03	0

[98] Private notes on lectures at Ohio State University, 1925.

B. REACTIONS OF THE COLLOIDAL MATTER OF CLAYS

Our investigations have shown that the reactions of the colloidal matter of clay are very similar to those of soaps;[97] that the conditions of solubility and insolubility are parallel, but that the colloidal matter of clay is probably more readily reacted upon. In either case we have a weak acid, only slightly soluble in the free state, the salts of which are all hydrolyzed and, excepting those of the alkalies and ammonium, only slightly soluble. Hence wherever, on addition of a reagent, exchange of bases is possible, the behavior exhibited by the clay will be akin to that of the corresponding soap. The fatty and soapy feel of highly colloidal clays so often mentioned by practical men as well as by writers on ceramics may be due to a real similarity rather than to a chance resemblance. This analogy with soaps is not inconsistent with the known facts about clays; it has proved a most helpful and suggestive guide in planning these investigations and it has never misled.

On the basis of this analogy some of the reactions exhibited by clays may be exemplified as follows:

(*a*) Excess of KOH or KCl added to the K-sol[98] reduces the solubility of the latter, giving rise to a gel. In this case, therefore, a salting-out effect produces coagulation.

(*b*) Addition of HCl or $CaSO_4$ to the alkali sol produces by exchange of bases the H or Ca compound, either of which, being less soluble than the original sol, appears as a gel. Here we have coagulation produced by exchange of bases.

(*c*) On the contrary, if NaOH or $Na_2C_2O_4$ is added to the H or Ca gels, the Na sol is regenerated; in other words, addition of such substance produces deflocculation.

In the actual case of a clay the reactions will be more complicated, owing to the multiplicity of possible reactions consequent upon the number of radicals present. Moreover, in accordance with the principle of mass action, the reactions will in general be incomplete. Their nature and extent is predicable from the solubility relations of the various possible solid phases. Unfor-

[97] Keppeler (Z. angew. Chem., 22, pp. 526–527; 1909) has noted a parallelism between the emulsification of fats by soaps and the effects produced upon clays by salts of acids of high molecular weight, but does not seem to have pursued the idea further. (See also Zsigmondy-Alexander, pp. 214–219.)

[98] This form of abbreviation is used for the sake of convenience to denote the sol which is formed by the action of water on a clay containing combined potash.

tunately, however, our knowledge of these relations is, if not lacking altogether, barely qualitative, far less quantitative, in character, so that in part we are forced to reason from analogy.

5. VARIETY OF CLAYS AND MINERALS TESTED

In this investigation use was made of as wide a range of clays as possible. English and American kaolins and ball clays, brick surface clays, sagger clays, peat, and surface clays containing much organic matter, shales, slate, No. 1 and No. 2 fire clays, and fuller's earth. The slate was least affected, shale next, and No. 1 fire clay next in order; the others were readily acted upon.

6. TIME REQUIRED FOR THE REACTIONS OF CLAYS

The reactions of clays are in general by no means instantaneous; usually a period of at least several hours is necessary for the attainment of the (comparatively) stable state assumed under any given set of conditions. This effect has been noted by various writers.

Thus Böttcher [99] found that, when alkali in excess of the proportion giving minimum viscosity was added to clays, the viscosity decreased with lapse of time, attaining a constant value in from 24 to 48 hours. This reliquefaction was accelerated by frequent shaking, and was accompanied by a decrease in the electrical conductivity of the liquid and in the concentration of alkali in the liquid. Moreover, it was not due to any action of carbon dioxide. Böttcher considered this effect to be a mechanical absorption of the alkali by the clay which by decreasing the alkali concentration would cause it to approach more nearly to the proportion giving minimum viscosity. According to the views expressed in this paper, it is to be attributed to a metathetical reaction between the clay and the alkali, a reaction which requires an appreciable time for its completion.

Morse and Curry [100] made numerous tests on this time effect and found that, while most of the change took place within an hour or two, some was still observable after 72 hours.

Similar results were obtained with many reagents in the course of the present work. For example, it was found that the amount

[99] Sprechsaal, 42, 1907, passim.

[100] 24th and 25th reports N. H. Agr. Expt. Sta., p. [illegible], 1915. See also Wo. Ostwald, Kolloidchemie, 412, 1927.

of calcium hydroxide required to keep some clay in suspension increased rapidly with the duration of contact with the clay.

Weber [101] found that casting slip, though perfectly fluid during the stirring operation, would occasionally on standing thicken to a gelatinous mass. He attributed the effect to the action of salts, especially sulphates and carbonates. This is doubtless true; the time effect being in part the slow solution of such slightly soluble substances as gypsum, which then gradually react with the clay. But it may also be due in part to a slow reaction between free silica of the clay and the alkali present.

Böttcher [102] has used measured amounts and concentrations of ammonia and of the hydroxides and carbonates of the alkalies to deflocculate equal weights of a stoneware clay. He made casting slips and determined their viscosity with an efflux viscosimeter with an orifice of 2 mm; he then diluted a portion of his slip in test tubes, obtaining series similar to those described in the present paper, but he did not measure the bulk of the sediments. He found a minimum of viscosity of the thick slip to coincide with a maximum of suspension of the diluted slip in the test tubes. This observation serves to show that the effect of the reagent depends less upon its concentration in the liquid medium than on the relative amounts of reagent and clay; moreover, it is good evidence that viscosity is not the main factor in suspension.

7. EFFECT OF CONCENTRATION OF THE REAGENT

That the concentration of reagent in the solution may be of less importance in determining the final state of the system than the ratio of reagent to clay is a point deserving further attention.

This is illustrated by the following table, which contains the results of tests made on Albert Lea Brick & Tile Co. yellow clay (Minnesota) with 0.1 molar sodium oxalate, the total volume being always 100 cc.

Weight of clay	Amount of reagent giving maximum suspension	Amount of reagent per gram clay
grams	cc	cc
20	60	3.0
5	13	2.6
1	11	11.0
0.1	11	110.0

[101] British Patent No. 6566; Mar. 18, 1909.

[102] Sprechsaal, 42, 1909; passim.

From this table it appears that with the larger amounts of clay the predominating factor is the ratio of reagent to clay; but with the smaller amounts of clay it is the concentration of reagent in the solution.

This behavior is entirely in accord with the views expressed in this paper and is directly attributable to the various solubility relations. If these were known approximately, the behavior of the system clay-reagent-water could, we believe, be roughly predicted for all ratios of the components.

8. OBSERVATIONS ON THE ACIDITY OF CLAY EXTRACTS

With reference to the acidity of soil extracts, Cameron and Bell [103] write:

> Soil extracts are usually either neutral or faintly acid to litmus. On boiling in platinum vessels, however, to eliminate carbon dioxide or possibly other volatile acids, in the vast majority of cases the solution will show an alkaline reaction with iodeosin, phenolphthalein, or litmus.

According to Morse and Curry:[104]

> The water extracts of soils seldom react acid * * * the water-bath residues of the water extract of soils are nearly always alkaline to phenolphthalein * * *. Most clay, clay soils, and muck, and some other soils, yield acid solutions when extracted with salt solutions.

And again:

> A clay, practically free from organic matter, came to our notice. The water extract of this clay was neutral to methyl orange, litmus, and phenolphthalein, and the clay itself decidedly acid toward litmus. Also when this clay was treated with sodium chloride for a quantitative estimation of its acid content, a strongly acid solution was obtained * * *. The large amount of acid in solution was decidedly at variance with the amount of organic matter in the clay.

The inference from these statements is that carbon dioxide is largely responsible for the apparent acidity of clays and soils. But carbon dioxide will hardly account for the increased acidity on addition of a salt, e. g., sodium chloride; this can be due only to the liberation of hydrochloric acid as the result of a metathetical reaction between the salt and the clay. This serves to confirm the view, repeatedly expressed in this paper, that the behavior of clays is conditioned largely by the possibility and occurrence of such metathetical reactions.

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[103] U. S. Dept. of Agr., Bureau of Soils, Bull. 30, p. 14; 1905.

[104] 19th and 20th reports N. H. Agr. Expt. Sta., pp. 271–272; 1908.

It was conjectured that there might be some relation between the plasticity of a clay and its acidity. Consequently the acidity of the cold-water extracts of a large number of clays was determined by the indicator method, using the series of indicators as given by Salm.[105] The acidity of the water extracts as determined in this way varied all the way from a concentration of hydrogen ion of about 10^{-3}, through neutral solutions, down to values of about 10^{-11}; but no relation between acidity of the extract and the plasticity or other qualities of the clay could be detected.

The results (in many cases of several determinations with that particular clay) are brought together in the following table:

Acidity of Water Extracts from Various Clays and Minerals

Hydrogen ion concentration[106]	Variety of clay	Hydrogen ion concentration	Variety of clay
10^{-3}	Jas. P. Prall, New Jersey, sagger clay, crude or dialyzed	10^{-5}–10^{-6}	Johnson Porter Clay Co., Tennessee ball No. 9
	Edgar Bros., New Jersey, No. 10 sagger	10^{-6}–10^{-7}	Brunt Mesaba iron ore
	Pike's No. 20, English ball		Groveport, Ohio, surface clay
10^{-3}–10^{-4}	Mandle-Sant Clay Co., Tennessee ball No. 3		Canton, Ohio, shale
10^{-4}	Geo. Knowles & Sons, No. 15 English china		Potter's "flint," (ground sand rock)
	Hammill & Gillespie A I English china		Fine white mica
	Champaign, Ill., joint clay		Fuller's earth (Eimer and Amend and R. J. Waddell)
10^{-4}–10^{-5}	Hall Clay Co., Georgia kaolin		Johnson Porter Clay Co., Tennessee ball No. 10
	Harris Clay Co., Penland, N. C., kaolin		Albert Lead, Michigan, yellow clay
	Edgar Bros. Co., Florida kaolin		Fort Pierre, South Dakota, sticky clay
	J. Poole, No. 1 English china	10^{-7}–10^{-8}	Edwards County, Tex., white fire clay
10^{-5}	Geo. Knowles & Son, No. 12 English ball	10^{-8}	Highland Fireclay Co., Missouri, No. 1 fire clay
	W. H. Wynn, Pennsylvania No. 1 and No. 2 fire clay		Owl Clay Co., Florida, fuller's earth
10^{-5}–10^{-6}	Diamond Clay Co., Ohio, No. 2 fire clay	10^{-8}–10^{-9}	Athens, Ohio, red fire clay
	Aluminum Co. of America bauxite		Peoria, Ill., joint clay
	Atlanta Mining & Clay Co., Georgia kaolin	10^{-9}	Brandywine Summit, Pa., soda feldspar
			Herron Lake, Minn., surface clay
			Albany, N. Y., slip clay
		10^{-9}–10^{-10}	Maine Feldspar Co., potash feldspar
		10^{-11}	Wyoming bentonite
			Calcined aluminum hydroxide

[105] Zs. physik. Chem., 63, pp. 83–108; 1908. It may be observed that a special investigation would be necessary in order to determine just in how far the application of this method is justifiable in determining the acidity of clay extracts. For instance, exchange of bases might well take place between the indicator (which is usually a salt) and particles of clay substance contained in the extract; if such a reaction took place, the indicator test would probably be quite misleading.

[106] See footnote 105.

Three of the most plastic clays of the table (Prall sagger, Tennessee No. 3, and Pike's No. 20 ball) give strongly acid extracts; on the other hand, the moderately plastic kaolins have about the same acidity as some of the highly plastic clays.

The clays investigated with respect to the acidity of their water extracts may be grouped roughly as follows:

Cracking clays: Neutral, but showing a considerable range on either side of the neutral point.

Fuller's earths, quartz, mica: Neutral.

Fire clays: Showing considerable range, but tending to be slightly acidic.

Shales: Weakly acidic.

Kaolins: Somewhat more strongly acidic.

Ball and sagger clays: Still more acidic, in general, though some of them range down to neutral.

C. EXAMINATION OF AN INSOLUBLE KAOLIN

A series of tests were made on the Georgia sagger clay (kaolin) of the Hall Clay Co. Its relative colloid content is 26, as compared with Tennessee ball clay No. 3 taken as 100.[107] The acidity of the clear aqueous extract was about 10^{-5} N, as determined by the indicator method.

Five gram portions of the clay were rotated for one hour with (*a*) 98 cc water, (*b*) 97 cc water and 1 cc HCl (specific gravity 1.20), and allowed to settle overnight. Qualitative tests on the clear liquids showed that the water soluble salts were mainly calcium sulphate and a trace of alkali chloride. Decidedly more calcium salt was present in the acid extract, indicating that a certain amount of replacement had taken place.

9. EFFECT OF REPEATED EXTRACTION WITH WATER

Into each of four glass-stoppered 100 cc graduated tubes was put 5 g of the clay with 98 cc distilled water, making a total volume of 100 cc. The tubes were rotated on the shaking machine for 1 hour; after standing for some time each contained 81–83 cc of clear liquid and 19–17 cc of sediment. Seventy-five cc of the clear liquid was siphoned off, replaced by water, the tube shaken, and allowed to stand overnight. This process was repeated until

[107] See U. S. Geol. Survey, Bull. 388, p. 49; 1909; cf. p. 41.

an equivalent dilution of 8000 times the original had been reached. It was found that the bulk of sediment increased somewhat with dilution. This is in agreement with the observations that the sediment becomes bulkier on prolonged contact with water and indicates that the amount of colloidal material increases under these conditions.

10. EFFECT OF ADDITION OF SODIUM HYDROXIDE TO THE CLAY AFTER REPEATED EXTRACTION WITH WATER

After a dilution of 8000 times had been reached the tubes were treated as follows:

Tube	A	B	C	D
Removed liquid (cc)	1	5	10	30
Added 0.1 *N* NaOH (cc)	0.1	1	5	10
Total volume (cc)	99	96	95	80

The tubes were then shaken for one hour and allowed to stand overnight, when readings were made. Successive additions of reagent were made,[108] as specified in the following table, in which the results are brought together.

TABLE I

Hall Clay Co. Georgia Sagger Clay (Kaolin). Effect of Addition of NaOH to the Clay, Previously Extracted Repeatedly with Water

Tube	A					B				C				D			
Total additions (in cc) of 0.1 *N* NaOH	0	0.1	0.3	0.5	0.7	1	2	3	4	5	7	8	10	10	15	20	30
Clear	81	80.5															78
Turbid [109]			79.5	5	2	1	1	([109a])	1	1	3	2	12	60	64	68	
Deeply turbid												74	64.5				
Dense				84	92	88.5	91	93.5	93	85.5	71.5						
Sediment	19	19.5	20.5	11	6	5.5	5	4.5	5	8.5	19.5	22	23.5	20	21	22	22

[108] In each case the reading was taken after the tubes had again been shaken for an hour and allowed to stand overnight.

[109] In this and the other tables turbid signifies that objects can still be detected through the liquid; deeply turbid, that objects can no longer be detected, but light is very evidently transmitted; dense, that little, if any, light is transmitted.

[109a] Trace.

The above results are considered to be due to a replacement by sodium of (1) any acid hydrogen (2) of the calcium in the original gel; this results in the formation of the sodium sol, which, however, is salted out again at the higher concentrations of alkali, thus accounting for the later increase in bulk of the sediment and for the final clarification of the liquid.

When the clay had not been previously extracted with water, its behavior in presence of soda was almost the same as the above, as might be expected from the nearly complete absence of soluble salts.

A similar series of experiments was performed with samples of this clay which had been repeatedly extracted with hydrochloric acid. Into each of four tubes was put 5 g clay along with 1 cc concentrated hydrochloric acid and 97 cc water. These were shaken one hour, allowed to settle, decanted, and refilled, this series of processes being repeated until a dilution of 8000 times the original volume of liquid was reached. The liquid over the clay was brilliantly clear at all stages of the dilution. Then successive additions of 0.1 *N* NaOH solution were made exactly as in the series presented in Table I, with results which are brought together in Table II.

TABLE II

Hall Clay Co. Georgia Sagger Clay (Kaolin). Effect of Addition of NaOH to the Clay Previously Extracted Repeatedly with HCl

Tube	G				H		
Total additions (in cc of 0.1 *N* NaOH)	0	0.1	0.3	0.5	1	2	3
Clear	72.5	71	77	74	71	.....	.....
Turbid	.....	.....	.....	.....	.....	1	1
Deeply turbid	.....	.....	.....	.....	.....	.....	.....
Dense	.....	.....	.....	.....	.....	90.5	92
Sediment	27.5	28	22	26	25	5.5	8

Tube	I			J					
Total additions (in cc of 0.1 *N* NaOH)	5	7	8.5	10	15	20	1000 30	1000 50	1000 75	1000 100
Clear	.....	.....	.....	.....	.....	.....	.....	.....	.....	85.5
Turbid	1	1	1	1	1	2	20	51	81	.....
Deeply turbid	.....	.....	.....	.....	.....	.....	64	27	.....	.....
Dense	89	91	92.5	73	78.5	88	.....	.....	.....	.....
Sediment	5	5	5	6	5.5	?	16	23	21	17.5

[1000] These additions were made with 2.5 *N* NaOH, so that the total volume should not be unduly increased.

As was to be expected, this behavior is practically identical with that of the clay extracted with water. For, according to our interpretation, the action of the hydrochloric acid can only be a replacement by hydrogen of the bases originally present; this process leaves the gels as such, because the solubility relations of the H-compound are similar to those of the compounds with the

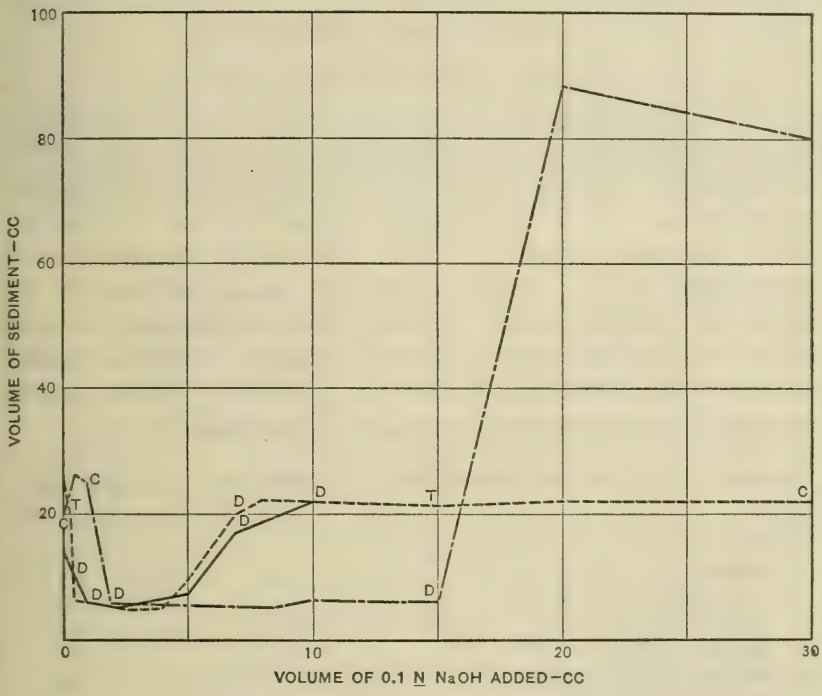

Fig. 1.—*Effect of additions of NaOH to kaolin (Georgia sagger clay, Hall Clay Co.)*

Cf. Tables I and II. —— Untreated; - - - - extracted with water; — - — - repeatedly extracted with dilute HCl, followed by water. The letters refer to the appearance of the supernatant liquid; C=clear, T=turbid, D=dense.

alkaline earths. For this same reason, the action of soda upon the H-gel is similar to its action upon the gels originally present. In other words, extraction of this particular clay with hydrochloric acid is without apparent effect upon its subsequent behavior in presence of solutions of sodium hydroxide. The behavior of this clay is more plainly shown in Fig. 1.

D. EXAMINATION OF A SOLUBLE CLAY

A similar investigation was made of the No. 1 light sagger clay of James P. Prall, Woodbridge, N. J. This clay closely resembles J. R. Cutter's No. 1 sagger clay and P. L. Ryan's No. 1 sagger clay, and behaves in many respects like Geo. Knowles & Sons' No. 12 English ball clay.

11. NATURE OF THE SOLUBLE SALTS

In this case the soluble salts were removed from the clay by a dialysis lasting two months, in which the water was changed 33 times, a total volume of about 16 liters being used. To prevent contamination with glass, the dialyzer was coated with paraffin and the extract was concentrated in a block tin pan. (In the following analysis tin and lead were determined and deducted.) The parchment paper used was treated for several days in the dialyzer to remove soluble sulphates before introducing the clay. The extract was analyzed by Mr. A. J. Phillips, analytical chemist in the Structural Materials Laboratory, with the following results, expressed as percentages of the weight of clay taken (50 g).

Analysis of the Dialyzed Extract of Jas. P. Prall, No. 1 Sagger Clay

	Per cent
Silica [110] (SiO_2)	0.091
Alumina (Al_2O_3)	.205
Ferric oxide (Fe_2O_3)	.149
Lime (CaO)	.085
Magnesia (MgO)	.001
Sulphuric anhydride (SO_3)	.174
Sodium oxide (Na_2O)	.033
Potassium oxide (K_2O)	.039
Organic matter	.064
Not determined (includes water, chlorine, etc.)	1.033
Total, dried at 110°	1.876

Qualitative analysis of the hydrochloric acid extract of this clay showed that its composition was similar to that of the water extract above.

[110] The occurrence of silica in the dialyzed extract is, at first sight, puzzling; but such an occurrence is quite usual, for Dr. Oswald Schreiner, of the Bureau of Soils, has assured the writer that in his dialyses a portion of the silica is invariably present in the extract. Indeed, this is to be expected.

EFFECT OF ADDITIONS OF SODIUM HYDROXIDE.

The effect of successive additions of NaOH on the behavior of this clay, both in the crude state and after dialysis, was tested in a way precisely similar to that just described for the Georgia sagger clay, except that a column of only 50 cc with 5 g of clay was used. The results are presented in Table III, and in part in Fig. 2, which shows the appearance of the tubes after they had been allowed to settle.

TABLE III

Sagger Clay (James P. Prall, Woodbridge, N. J.). Effect of Addition of NaOH to the Clay (A) in the Crude State; (B) After Removal of the Soluble Salts by Long Dialysis with Water

(A)

Total addition (in cc) 0.1 *N* NaOH	Clear	Turbid	Dense	Sediment
0.1	43.6	.....	.....	6.4
0.4	43.8	.....	.....	6.2
0.7	43.3	.....	.....	6.7
1	42.6	.....	.....	7.4
2	.....	41.5	.....	8.5
3	.....	26.5	20	3.5
5	.....	2	44.8	3.2
6	.....	.....	46.6	3.4
8	.....	.....	47	3
10	.....	.....	47	3
16	.....	2.5	44.1	3.4
24	.....	4.4	44.1	1.5
32	.....	21.5	.....	28.5
50	.....	37.3	.....	12.7

TABLE III—Continued

(B)

Total addition (in cc) 0.1 *N* NaOH	Clear	Nearly clear	Turbid	Dense	Sediment
0	35.5				14.5
0.1		36			14
0.4			35		15
0.7			31		19
1				44.5	5.5
2				45.5	4.5
3				47	3
5				47	3
8				47	3
10				47	3
16				47.5	2.5
20				47.5	2.5
25				47.5	2.5

Total addition (in cc) 2.5 *N* NaOH	Clear	Turbid	Dense	Sediment
1.5			47	3
2		5	43	2
2.5		7	41	2
3		13	36	1
3.5		19	30	1
4	28.5			21.5
8	23			27

The table shows that there is a decided difference in behavior toward NaOH of the crude clay and of the clay from which the soluble salts have been removed.

In presence of the greater concentration of NaOH the liquid seemed to change to a thin jelly, which thickened as the concentration increased; concurrently the bulk of granular sediment seemed to shrink and finally almost to disappear. This is attributed to the fact that the thickening gel is able to hold in suspension progressively coarser grains, until finally gel and grains become intimately and uniformly mixed. On the diagram (Fig. 3) the total volume occupied by this mixture of gel and sediment is given by the line marked "recoagulated."

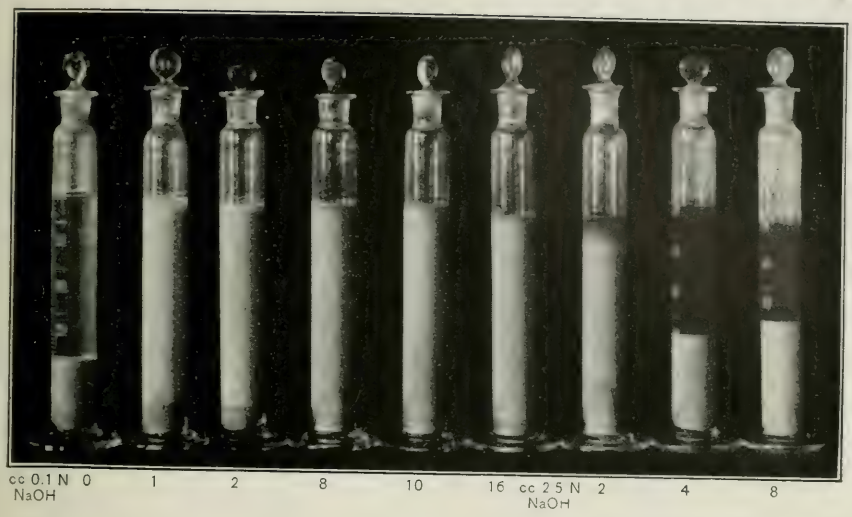

Fig. 2.—*Effect of additions of NaOH to a dialyzed sagger clay (No. 1, Jas. P. Prall, Woodbridge, N. J.)*

Cf. Table III and Fig. 3. In each tube 5 grams clay; amount of NaOH as given above. Photograph taken after the tubes had been allowed to settle

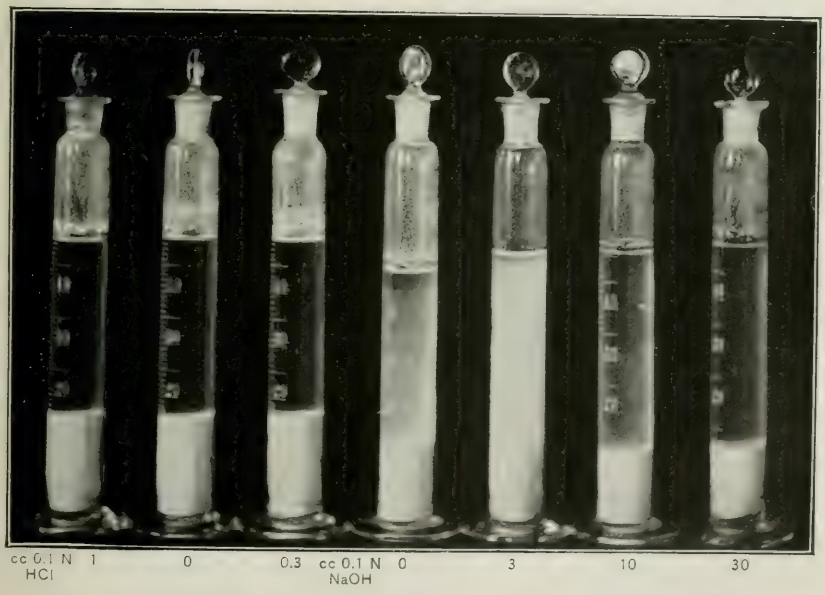

Fig. 5.—*Effect of additions of HCl and of NaOH to an English china clay (Hammill and Gillespie's A 1)*

Five grams clay in each tube; amount of reagent as stated above

13. SOLVENT ACTION OF SUCCESSIVE PORTIONS OF WATER

Unlike the Hall kaolin, the Prall sagger clay can not be freed of soluble salts by repeatedly shaking with water, settling, and decanting; for, after a few portions of water are removed, a portion of the clay goes into very permanent suspension.

An attempt was made to determine how much of this clay is removable by extraction with water. A 5-gram portion made up to 100 cc with water was shaken for an hour; after standing overnight, about 90 cc of the liquid was siphoned off and replaced by

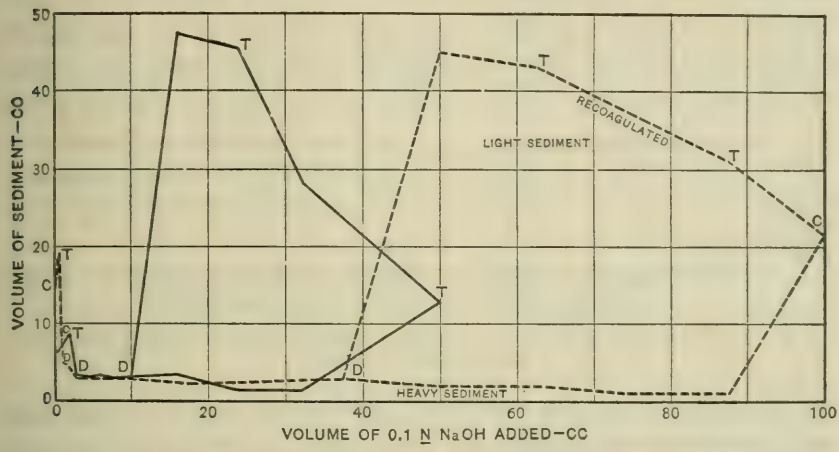

Fig. 3.—*Effect of additions of NaOH to a sagger clay (No. 1, Jas. P. Prall, Woodbridge, N. J.)*

Cf. Table III and Fig. 2. —— Untreated; - - - - Dialyzed. The letters refer to the appearance of the supernatant liquid; C=clear, T=turbid, D=dense.

fresh water. This process was repeated 62 times without any indication of approaching a clear extract.

The relative turbidity of each of these extractions was determined by pouring the liquid into a graduated Nessler tube provided with a stopcock near the bottom, shaking up the contents [111] to insure that the turbidity would be uniform from top to bottom, drawing off the liquid until the print of a newspaper placed beneath the tube could be read through the remaining liquid, and

[111] The necessity of shaking was established by a special experiment, which showed that the turbidity of a liquid which has remained undisturbed for some time may be three or four times as great at the bottom as at the top. Cf. Bodländer (Investigation of Suspensions I., Neues Jahrb. Min. 1893, II., p. 150), who writes: "For making comparable tests with suspensions which have stood quietly for a long time under definite conditions it is necessary that the test portions should always be taken from equal depths, because on long standing the amount of kaolin increases with the depth."

reading the depth of liquid at this point. The results are presented graphically in Fig. 4.

When the clay was shaken with the water for more than one hour a higher turbidity was recorded; when it was allowed to stand for a longer period than overnight (as when a Sunday intervened) a lower result was obtained. When the test was stopped, 3.5 grams clay still remained in the tube.

Fig. 4 shows that the highest turbidities were obtained in the earlier extractions, and that after a number of extractions the turbidity was approximately constant. This behavior is probably due to a gradual transformation of some of the crystalline silicates of the clay into the colloidal state, this being the source of the daily supply. These results agree with the figures given

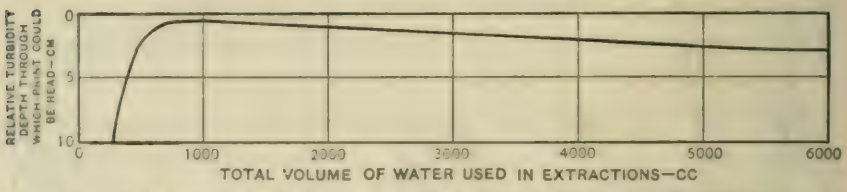

Fig. 4.—*Relative turbidity of the extracts obtained by repeated extraction of sagger clay (No. 1, Jas. P. Prall) with water*

by Parmelee [113] for the additional amount of clay removed with each extraction when using the centrifugal apparatus for mechanical analysis.

The action of varying amounts of water upon two clays was also investigated. One-gram portions of clay were mixed with portions of distilled water; after occasional shakings and settling for several weeks, measurements were obtained as recorded in Tables IV and V.

TABLE IV

Effect of Varying Amounts of Water on Crude Sagger Clay (Prall)

Volume of water and clay—cc	50	300	400	1,000
Clear	47			
Turbid		294	280	300
Deeply turbid			116	698
Sediment	3	6	4	2

[113] Trans. Am. Ceramic Soc., 11, pp. 479–480; 1909.

TABLE V

Effect of Varying Amounts of Water on a Surface Clay From Groveport, Ohio

Volume of water and clay	12.5	25	50	100	200	1,000
Clear	4.5					
Nearly clear		17				
Turbid			42,5		194	994
Dense				94		
Sediment	8	8	7.5	6	6	6

The relative turbidity of the 1000 cc liquid (Table V) was the same as that of the 50 cc liquid, indicating that in the former case there was about 20 times as much matter in suspension as in the latter. These results all show the increased formation of colloidal material attending the use of a greater bulk of water.

The idea that the suspensions produced by the action of water on clay are due not to the fineness of the original material directly but to the fine state of division of the matter produced by reactions between the water and clay, is in harmony with a number of observations. For instance, Hall and Monson [113] found that pure silica would remain turbid but a short time in water; on the other hand, we found that impure silica (ground sandrock) gave a fairly permanent suspension in water, attributable to the alterations, produced by the water, of the alkaline and other impurities of the sandrock.[114] These impurities would with comparative readiness be acted upon and transformed into the colloidal state; whereas the silica itself is very inert, and in contact with water under ordinary conditions is transformed only to an inappreciable extent. Moreover, Atterberg,[115] from experiments on the influence of various substances (saturated $Ca(OH)_2$ soln., 5 per cent solns. of HCl and NaCl) on the rate of sedimentation of sand grains of various sizes, concluded:

> A distinctly visible formation of floccules, as with the coagulation of clay water, is not shown, even with the finest sand grains (0.002–0.001 mm) isolated by me. Flocculation visible to the eye appears to occur only with still finer particles of matter, with the colloids.

[113] J. Agr. Sci., 2, p. 246; 1907. [114] See Fig. 24. [115] Landw. Vers. Sta., 69, p. 134; 1908.

This is confirmed by Schloesing,[116] who found that addition of an alkaline-earth salt or of an acid produced no effect on the sedimentation in distilled water of suspensions of fine sands free from colloid matter.

All of these observations indicate that the coagulation or sedimentation is not a mechanical effect, but is due to the occurrence of a reaction the product of which settles out.

EFFECT OF VARYING THE TEMPERATURE OF THE WATER

On the basis of the views advanced in this paper we should expect that rise of temperature would cause differences of behavior. For instance, the action of water should be more pronounced at higher temperatures. This effect is illustrated by the following experiments:

(*a*) A 50-gram portion of X Wad Clay (Johnson-Porter Clay Co., Tennessee) was deflocculated with 70 cc 0.1 *N* NaOH and elutriated in the Schulze apparatus with water at various (constant) temperatures. The percentage residue on the 120-mesh sieve in each case and in the overflow is given below.

(*b*) A similar elutriation was made with feldspar (Maine Feldspar Co.) without previous treatment with alkali.

TABLE VI

Influence of Varying the Temperature of the Water in Elutriations with the Schulze Apparatus

(*a*) DEFLOCCULATED X WAD CLAY

Temperature of water	On 120-mesh sieve	Can 1	Can 2	Can 3	Overflow
Degrees					
10	3.06	21.14	21.78	7.46	46.11
15	2.32	21.84	21.18	5.18	49.03
25	2.26	24.44	14.98	3.74	54.13
35	2.08	29.96	6.16	3.60	60.75
40	2.24	26.86	1.68	5.44	63.33

(*b*) FELDSPAR

Degrees					
17		13.14	29.04	7.98	49.24
40		18.22	4.06	3.62	74.10

[116] Chimie Agricole, in Fremy's Encyclopédie Chimique, p. 68, 1888.

Now we should expect that at higher temperatures the carrying capacity of the water would be smaller if anything, on account of the diminution of density and of viscosity; yet we find a decreased aggregate residue in cans 2 and 3 and a great increase in the amount carried off by the overflow. This shows that the average size of the particles was smaller the higher the temperature, which indicates an increase in the action of water with the temperature; presumably, therefore, an increased rate of solution and a greater amount dissolved.

F. GENERAL BEHAVIOR OF CLAYS TOWARD REAGENTS

The standpoint adopted in the present paper is that the behavior of a clay toward a reagent is determined by the possibility of a more or less complete metathetical reaction between them; the actual result in each case depending on the form or state in which the product (or products) of a particular reaction appears. In other words, the behavior toward reagents is determined by the solubility relations of the possible solid phases; the clay "solution" is then the suspension of the products of reaction, not of the unaltered clay.

Before proceeding to a detailed account of the action of various substances we shall present additional evidence in favor of the above point of view and of its superiority to some of the other hypotheses which have been put forward to correlate some of the effects observed.

This point of view was advocated by Hall and Monson,[117] who state that "soluble salts such as cause flocculation merely interchange bases with the complex hydrated double silicates which make up kaolin."

They give the following table showing the comparative power of flocculating kaolin suspensions possessed by equivalent (about 0.001 *N*) solutions of salts, acids, and bases (the alkalies and most alkaline substances act as deflocculants).

[117] J. Agr. Sci., 2, pp. 244–256; 1907.

SALTS		ACIDS		BASES	
$Al_2(SO_4)_3$	20	HCl	20	$CaH_2(CO_3)_2$	10
$CaCl_2$	>10	HNO_3	19	$Ca(OH)_2$	3
$Ca(NO_3)_2$	10	H_2SO_4	13	$Ba(OH)_2$	3
$Ba(NO_3)_2$	10	Acetic acid	9		
$CaSO_4$	> 5	Oxalic acid	2.5		
$MgSO_4$	< 5	Tartaric acid	2.5		
KCl	> 2	Carbonic acid	0.5		
KNO_3	> 2	Citric acid	0		
NaCl	> 1	Phenol	0		
K_2SO_4	< 1				
$NaNO_3$	< 1				
Na_2SO_4	0.5				

The general character of these results is such as we might anticipate if coagulation were the sequel of a chemical reaction; on any other theory it would be hard to account for the similarity of effect shown by substances which would be expected to show similar chemical reactions with the constituents of clays. Considerable evidence in favor of these views has already been presented (p. 22 et seq.); the following may also be given. Gorgeu [118] found that kaolin would displace (though not, of course, completely) carbonic acid and chlorine from alkali carbonates and chlorides, respectively. J. Dumont [119] measured the amount of carbon dioxide gas set free when 1 cc N K_2CO_3 solution remained in contact with several colloids for periods varying from 2 to 66 hours. His results, expressed in mg CO_2 set free by the colloid, follow.

Hours	Noncolloidal fine sand 20 g	Plastic clay 4 g		Kaolin 4 g		Gelatinous silica 4 g	Ferric hydroxide 4 g	Aluminum hydroxide 4 g
		Normal	Calcined	Normal	Washed			
2	0.00	4.75	8.41	0.00	0.18	1.08	0.91	2.18
16	0.00	3.61	6.54	0.36	0.00	0.74	1.68	4.07
24	0.00	3.30	1.69	0.00	0.18	0.55	1.84	5.90
40	0.00	1.70	3.02	0.18	0.00	0.54	2.60	4.02
66	0.00	2.62	1.32	0.00	0.00	0.36	2.77	3.64
Total	0.00	15.98	20.98	0.54	0.36	3.27	9.80	19.81

[118] Ann. chim. phys. [6], **10**, p. 145; 1887.

[119] Compt. rend., **142**, p. 345; 1906.

According to the views here advocated, any reaction which is accompanied by a net decrease in solubility of the various components produces an increase in the degree of flocculation; conversely, any reaction which results in products somewhat more soluble than the original constituents produces more or less deflocculation.

Now, it has been asserted by Foerster [120] and by Rohland [121], apparently independently, that the concentration of hydroxyl ion is the essential factor in effecting the deflocculation of clays. It is without doubt one of the factors, in the same way that every condition affects the degree of flocculation to some extent; but the following evidence, we believe, demonstrates that the concentration of hydroxyl ion is relatively a very unimportant factor in promoting this deflocculation.

14. CONCENTRATION OF HYDROXYL ION A MINOR FACTOR IN PROMOTING THE DEFLOCCULATION OF CLAYS

The following tests were made on 5-gram portions of No. 2 fire clay (W. H. Wynn & Co., West Decatur, Pa.) in the way described previously (p. 48); varying amounts of (*a*) oxalic acid, (*b*) potassium oxalate, (*c*) ammonium oxalate, were added, and determinations were made of the amount of clay in suspension and of the concentration of hydroxyl ion.

[120] Die chemische Industrie, 28, [24], pp. 733–740; Dec. 15, 1905. [121] Z. anorg. Chem., 41, p. 325; 1904.

TABLE VII

Deflocculation of a No. 2 fireclay

(*a*) ADDITION OF 0.1 MOLAR OXALIC ACID

cc added	0	0.05	0.1	0.2	0.3	0.5	1	1.5	2	[illegible]
Turbid	42	7	5	4	3	6	15	43	42.5	42.5
Deeply turbid							28			
Dense		36	40	40	41	37				
Sediment	8	7	5	[illegible]	6	7	7	7	7.5	7.5
−log OH′ [12]	9	9	10	10	10	10	10.5	11	11	11

(*b*) ADDITION OF 0.1 MOLAR POTASSIUM OXALATE

cc added	0	0.5	1	3	7	10	15	20	30	48
Clear								42.5	42.5	42.5
Nearly clear	42.7						43			
Turbid		3	3	4	43.5	43				
Dense		41.5	42	40						
Sediment	7.3	5.5	5	6	6.5	7	7	7.5	7.5	7.5
−log OH′	9	9	[illegible]	7	7	6.5	6.5	6.5	6.5	6.5

(*c*) ADDITION OF 0.1 MOLAR AMMONIUM OXALATE

cc added	0	0.5	1	3	6.5	10	20	30	[illegible]	
Clear									93.7	
Nearly clear								93.3		
Turbid	93	7	6	6	94	93.5	93.5			
Dense	7	88.8	89.5	89.5						
Sediment	7	4.2	4.5	4.5	6	6.5	6.5	6.7	6.3	
−log OH′	9	9	[illegible]	7	7	6	6	6	6	

[12] The hydroxyl ion concentrations are given in this way for the sake of clearness. This is, of course, merely another way of stating that the concentration of OH′ is 10^{-9}, etc. The values given may be considered as logarithms of the *dilution* of OH′.

From the above table it is evident that the maximum of suspension occurs at different concentrations of hydroxyl ion; In (*a*) at 10^{-10}, in (*b*) at 10^{-9}; and in (*c*) about 10^{-8}.

Analogous results were obtained on treating kaolin with various reagents. The following table, which gives the maximum of suspension with 5-gram portions of Harris Clay Co., Penland Kaolin (North Carolina), renders it evident that the concentration of OH′ is certainly not the essential factor.

TABLE VIII

The Hydroxyl Ion Concentration and the Maximum Deflocculation of Kaolin

Volume of reagent giving maximum cc	Reagents (each 0.1 molar)	−log OH′	Volume of sediment cc
48 or 98	Pure water	9	12
0.2	Oxalic acid	9	11
0.4	Sodium-dihydrogen phosphate, NaH_2PO_4	9	8.5
0.5 to 20	Sodium silicate	3–9	6
0.4 to 2	di-sodium-hydrogen phosphate, Na_2HPO_4	6–8	7.5
3	Sodium oxalate, $Na_2C_2O_4$	7	5
3	Potassium oxalate, $K_2C_2O_4$	7	6
3	Ammonium oxalate $(NH_4)_2C_2O_4$	7	6.3
10	Aniline	7	9
0.4 to 10	Tri-sodium phosphate, Na_3PO_4	2–7	7
1	Lime, $Ca(OH)_2$	6	10
1	Barium hydroxide, $Ba(OH)_2$	5–6	7
1	Potassium cyanide, KCN	6	7
3	Sodium sulphide, Na_2S	6	6.5
3 to 30	Sodium carbonate, Na_2CO_3	3–5	6
4	Sodium hydroxide, NaOH	3	5.5
4	Potassium hydroxide, KOH	2–3	7

The foregoing evidence is, we believe, conclusive against the idea that the concentration of hydroxl ions is the essential factor in promoting deflocculation; but it in no way conflicts with the idea that the degree of flocculation is conditioned by the relative solubilities of the various possible solid phases, and that the concentration of OH′ is merely one of the minor factors affecting the solubility, and possibly also the degree of dispersion, of the various substances.

We shall now consider in greater detail the behavior of clay toward a number of reagents.

15. DEFLOCCULANTS

The principal deflocculants are solutions of the alkalies and of salts which by hydrolysis are alkaline; but, as we shall see, other substances may also exert a deflocculating effect. The behavior of clay in contact with sodium hydroxide (Fig. 5, plate facing p. 54) is similar to that observed with the other alkalies, but the effect

of potassium hydroxide and ammonium hydroxide are progressively weaker (Figs. 6, 7, 8, 9). The latter can exert a coagulating effect only at the highest concentrations.

The mechanism of the action of alkalies upon clay we conceive to be somewhat as follows: The alkali reacts with the constituents of the clay and forms an alkali silicate or aluminosilicate, which in solution is hydrolyzed to some extent, so that part of it is present as a sol. Further addition of alkali increases the amount of sodium

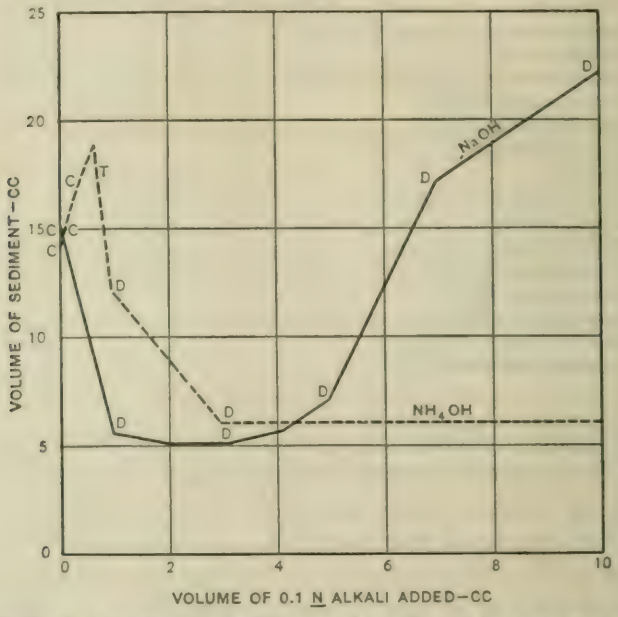

Fig. 8.—*Comparison of the effects of additions of NaOH and of NH_4OH to Georgia kaolin (Hall Clay Co.)*

Five grams clay; total volume 100 cc. Letters refer to the appearance of the supernatant liquid; C=clear, T=turbid, D=dense.

salt in solution and in the sol state up to a certain point at which an increase of the alkali concentration begins to set back the hydrolysis and to cause a diminution in the amount of sol. This process goes on progressively until at a certain concentration most of the clay is again coagulated. On this view we should expect the effect of potassium compounds to be less than that of the corresponding compounds of sodium, for the salts of the former are usually the more soluble, while the still weaker effect of

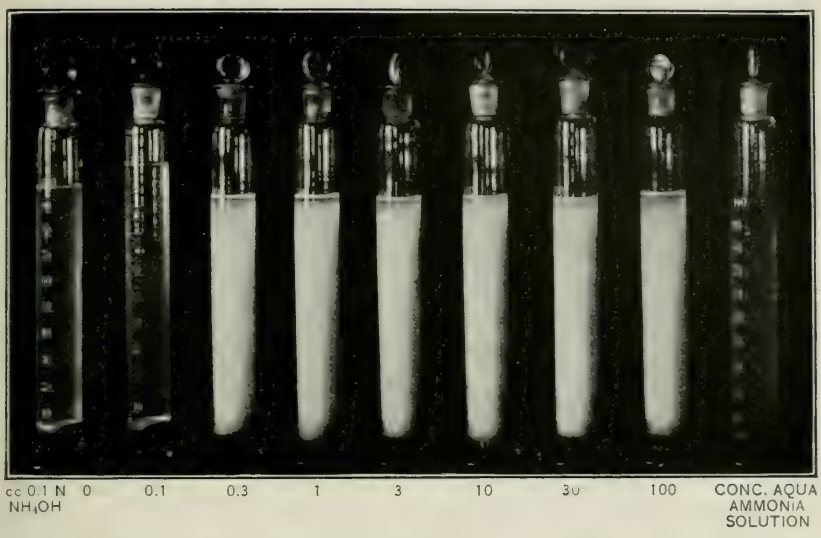

Fig. 6.—*Effect of additions of NH_4OH to a fire clay (No. 2 Diamond Clay Co., Nelsonville, Ohio)*

In each tube 5 grams clay; amount of NH_4OH as given above

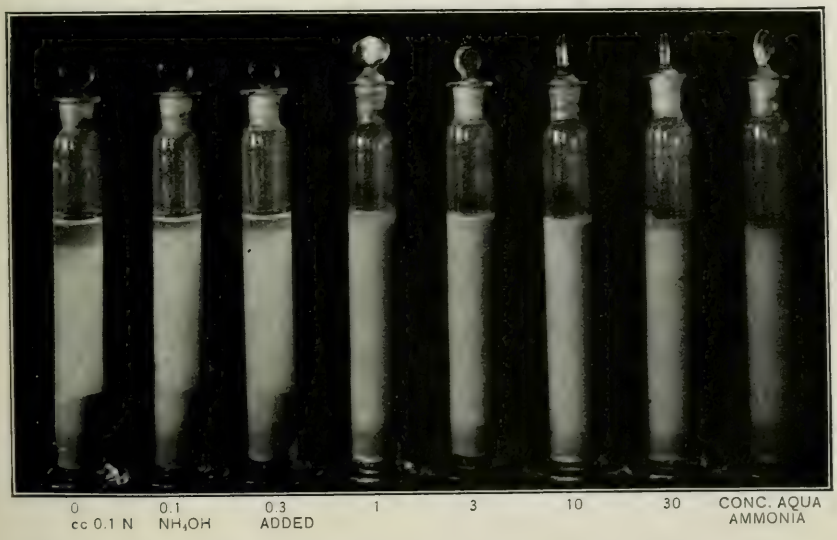

Fig. 7.—*Effect of additions of NH_4OH to a Tennessee ball clay (No. 9, Johnson-Porter Clay Co.)*

In each tube 5 grams clay; amount of NH_4OH as given above

ammonia is due to its weakness as a base, wherefore it can not set back the hydrolysis and so cause recoagulation except at the greatest concentrations.

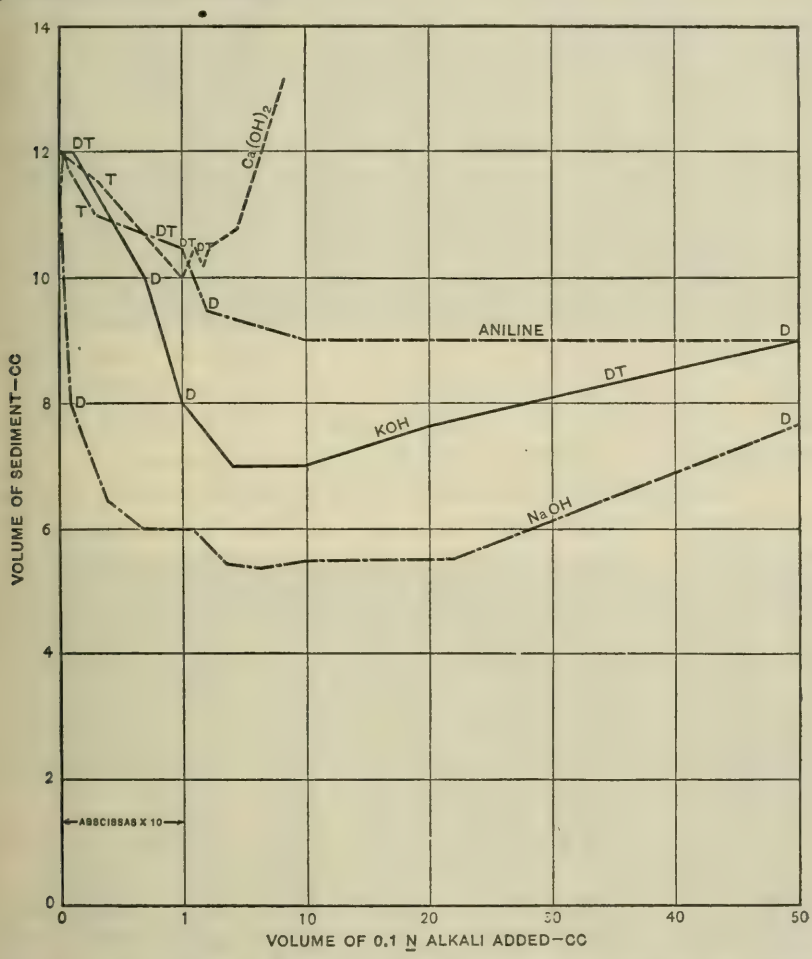

Fig. 9.—*Comparison of the effects of additions of various alkalies (NaOH, KOH, aniline, $Ca(OH)_2$) to kaolin (Harris Clay Co., Penland, N. C.)*

Five grams clay; total volume 50 cc. Letters refer to the appearance of the supernatant liquid; T=turbid, DT=Deeply turbid, D=dense.

The mode of action of hydrolyzable salts is in part the same as that of the caustic alkalies; but another mode of action comes into play here, which occurs with all soluble salts, which (1) do not

give an acid reaction in aqueous solution, (2) contain an acid ion which gives an insoluble compound with bivalent and trivalent bases. This mode of action may be exemplified by sodium carbonate or oxalate, thus:

$$Na_2CO_3 + Ca\ gel \rightarrow CaCO_3 + Na\ sol$$
$$Na_2C_2O_4 + Ca\ gel \rightarrow CaC_2O_4 + Na\ sol$$

That is, we remove the bases which conserve coagulation (that is, form less soluble gels) by a double decomposition and form the more soluble alkali salt, thus promoting deflocculation. Addition of larger amounts of the salt may produce a recoagulation, which is caused by the diminution of solubility consequent upon the increased concentration of the common ion (salting-out action). Such added salts will also react with any soluble salts present with the clay; this may complicate matters and will render necessary the addition of a larger amount of salt than would be required for deflocculation if soluble salts were absent.

The following salts have been used as deflocculators in these experiments: Sodium oxalate, $Na_2C_2O_4$ (Fig. 10); potassium oxalate, $K_2C_2O_4$ (Figs. 11 and 13); ammonium oxalate $(NH_4)_2C_2O_4$; sodium silicate (Fig. 22); soft soap (Fig. 21); borax, $Na_2B_4O_7$ (Fig. 12); potassium phosphate, K_3PO_4; sodium phosphate, Na_3PO_4 (Fig. 13); disodium hydrogen phosphate, Na_2HPO_4; sodium dihydrogen phosphate, NaH_2PO_4; sodium-hydrogen-ammonium phosphate $NaHNH_4PO_4$; potassium cyanide, KCN; potassium ferrocyanide, $K_4Fe(CN)_6$; sodium arsenite, $NaAsO_2$; sodium sulphide, Na_2S (Fig. 13); potassium permanganate, $KMnO_4$.

With a given clay sodium carbonate is not necessarily the most effective of the group, although it is the most used industrially.

Fig. 13 shows the effect of several alkaline precipitants—trisodium phosphate, potassium oxalate, and sodium sulphide—on a No. 2 fire clay containing a considerable amount of soluble salts. It shows that the range within which complete deflocculation takes place is very narrow and that the salting-out action commences at once with further additions of reagent.

The manner in which calcium sulphate suppresses the deflocculating effect of an alkali is shown in Fig. 14. The clay used was a 5-gram portion of the Tennessee ball clay No. 3 of the Mandle-Sant

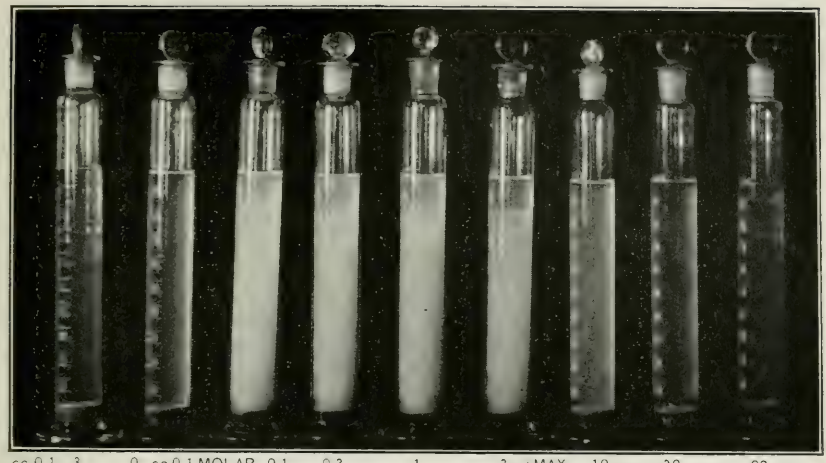

Fig. 10.—*Effect of additions of HCl and of sodium oxalate to flint fire clay (W. H. Wynn & Co., West Decatur, Pa.)*

In each tube 5 grams clay; amount of reagent as given above. Maximum deflocculation occurred with 7 cc 0.1 molar $Na_2C_2O_4$ solution

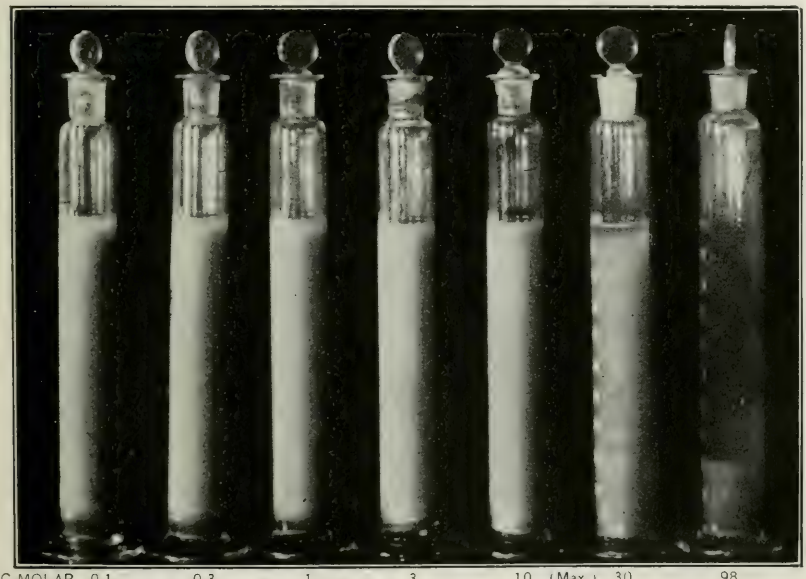

Fig. 11.—*Effect of additions of potassium oxalate to Tennessee ball clay (No. 3, Potters' Supply Co.)*

In each tube 5 grams clay; amount of reagent as given above. Maximum deflocculation occurred with 20 cc 0.1 molar $K_2C_2O_4$ solution

Clay Co.; the abscissas represent the amount of 0.1 *N* NaOH solution added; the ordinates are the additions of 0.1 molar $CaSO_4$.

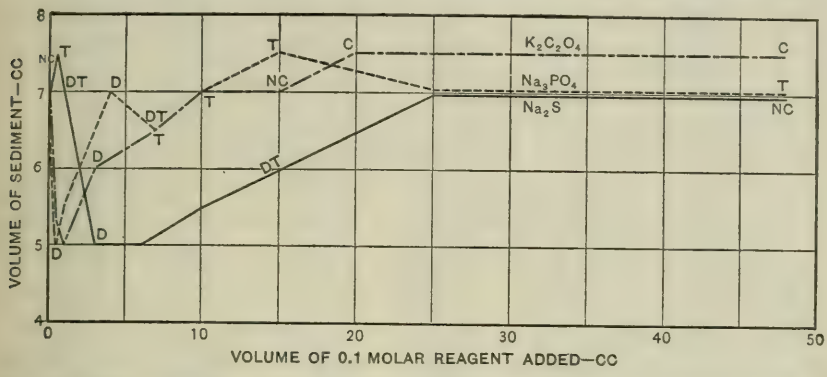

Fig. 13.—*Effect of additions of reagents (potassium oxalate, trisodium phosphate, sodium sulphide) to fire clay (No. 2, W. H. Wynn.)*

Five grams clay; total volume 50 cc. Letters refer to the appearance of the supernatant liquid; C=clear, NC=nearly clear, T=turbid, DT=deeply turbid, D=dense.

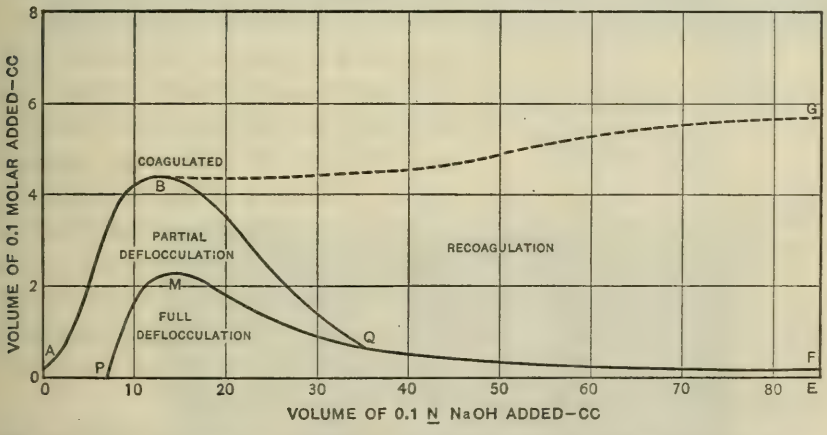

Fig. 14.—*Effect of simultaneous additions of NaOH and $CaSO_4$ to a ball clay (No. 3, Mandle-Sant Clay Co.)*

Five grams clay; total volume 50 cc.

The clay was partially deflocculated in water and was fully deflocculated when 7 cc NaOH had been added (point *P*); and further additions up to a total of 85 cc NaOH (point *E*) continued to keep all the colloid clay in suspension. About 0.2 cc $CaSO_4$ (*A*)

sufficed completely to coagulate the clay, with complete clarification of the liquid; and further additions up to a total of 8 cc $CaSO_4$ continued to keep the clay wholly coagulated. When both $CaSO_4$ and NaOH were added to the clay, the colloid matter was wholly deflocculated only with those quantities represented by points within the area *PMQFEP*.

In other words, with this clay slight additions of $CaSO_4$ very rapidly narrowed the range of concentrations of NaOH effecting deflocculation until 2.3 cc of the $CaSO_4$ solution limited full deflocculation to but one proportion of the NaOH solution, viz, 15 cc at the point M. Concentrations of $CaSO_4$ given by the line *ABG* wholly coagulated the clay and kept it at nearly the original bulk; larger amounts also kept the clay coagulated, but the bulk became gradually larger as the distance above the line *ABG* increased. In the area *QBGF* the clay was momentarily deflocculated as if by only 15 cc NaOH when the NaOH was first added; but when thorough mixture and full reaction was effected the clay was recoagulated. The bulk of the recoagulated clay was very large along the line *QF* and gradually decreased to the line *BG*, where it had nearly the original bulk. The area *ABQMP* represents proportions of $CaSO_4$ and NaOH with which the clay assumed an intermediate condition, partly coagulated and partly deflocculated.

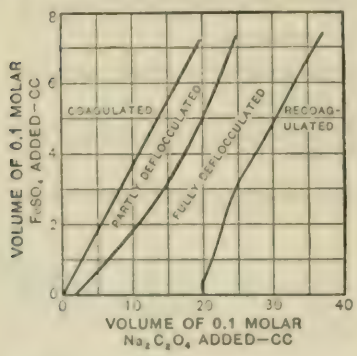

Fig. 15.—*Effect of simultaneous additions of $Na_2C_2O_4$ and $FeSO_4$ to a ball clay (No. 3, Mandle-Sant Clay Co.)*

Five grams clay; total volume 50 cc.

The effect of sodium oxalate in combating the coagulating effect of additions of ferrous sulphate to the same clay is shown in Fig. 15. The amount of sodium oxalate required for deflocculation is evidently almost strictly proportional to the amount of ferrous sulphate added; a certain additional amount, whatever the original concentration, effects recoagulation.

A few experiments were made with organic substances. Aniline acts as a very weak deflocculating agent. (See Fig. 9.) Glycerin appears to be without action on clays.

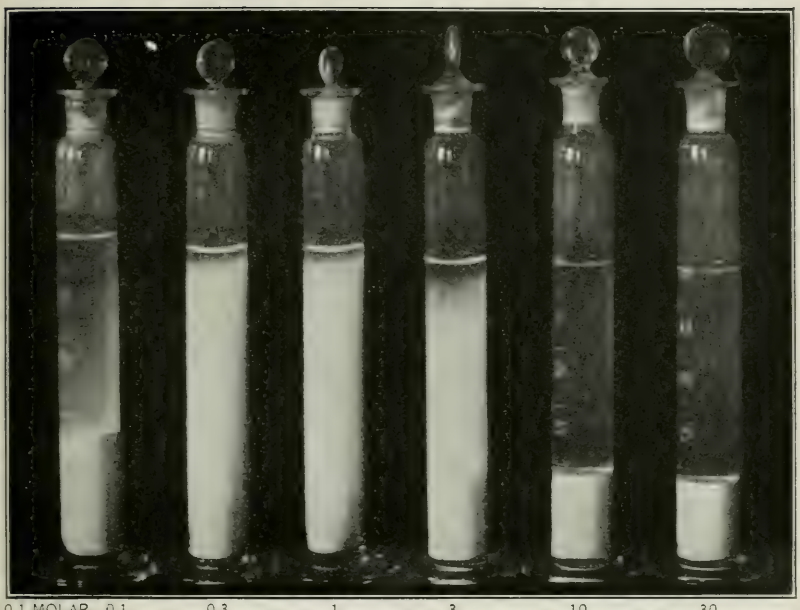

Fig. 12.—*Effect of additions of borax to English china clay (No. 1, J. Poole)*

In each tube 5 grams clay; amount of reagent as given above

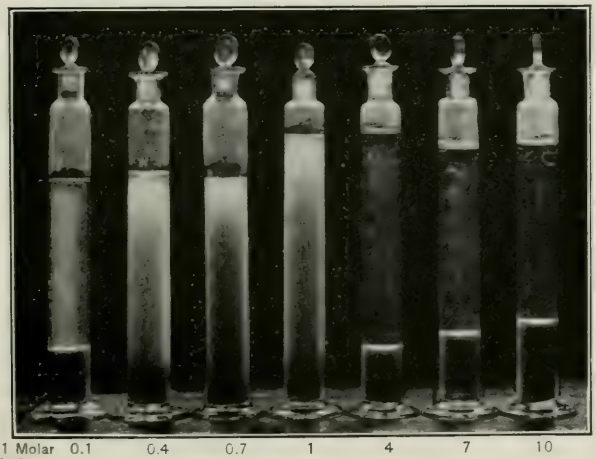

Fig. 16.—*Effect of additions of lime to English china clay (No. 1, J. Poole)*

In each tube 5 grams clay; amount of $Ca(OH)_2$ as given above

BIVALENT DEFLOCCULANTS.

Compounds of bivalent elements are in general coagulants; a few exceptions may be noted.

Hydroxides of Calcium and Barium.—The deflocculating action occasionally shown by calcium hydroxide or barium hydroxide (Figs. 16, 17, 18) is believed to be due to an action upon such soluble salts as Na_2SO_4 or $(NH_4)_2SO_4$, resulting in the formation of a deflocculating alkali, or possibly in some cases to an action by which the amount of coagulant with the clay is decreased. In this connection there is opportunity for further research.

In 1907 A. Lottermoser [123] said that barium hydroxide and calcium hydroxide show a decreasing effect (as compared with alka-

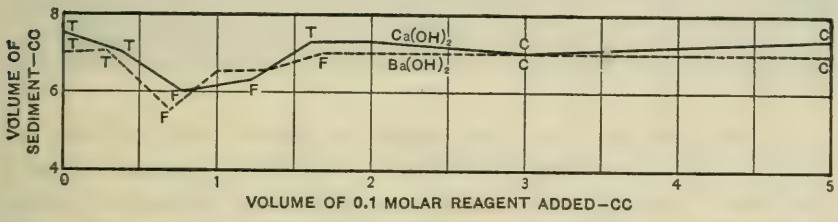

Fig. 18.—*Effect of additions of lime and of baruim hydroxide to a fire clay (No. 2, W. H. Wynn.)*

Cf. Table IX; C=clear, T=turbid. F denotes that the clay is deflocculated.

lies?) as hydrosol formers on clay. Notwithstanding this prior publication, in 1909 E. Weber [124] patented the addition to casting slips of calcium oxide (CaO), barium oxide (BaO) or peroxide (BaO_2), "which on contact with water will be converted into hydroxides; or of other compounds of the alkaline earths and lead which give insoluble sulphates and carbonates," in order to remove those compounds that interfere with the use of alkalies in preparing casting slips.

The following tables give the data obtained with barium hydroxide and with calcium hydroxide upon No. 2 fire clay. (See also Fig. 18.)

[123] Z. physik. Chem., 60, p. 456; 1907. [124] British Patent No. 6560 (Mar. 18, 1909).

TABLE IX

No. 2 Fire Clay from W. H. Wynn, Decatur, Pa. (5 grams)

(*a*) ACTION OF 0.1 MOLAR $Ba(OH)_2$

cc added	0	0.3	0.7	1	1.3	1.7	3	7	15	30
Clear							43	43	43	43
Turbid	43	43	7	7	10	13				
Dense			37.5	36.5	33.5	30				
Sediment	7	7	5.5	6.5	6.5	7	7	7	7	7

(*b*) ACTION OF 0.1 MOLAR $Ca(OH)_2$[124a]

cc added	0	0.4	0.8	1.2	1.6	2	3	5	8	10
Clear							93	92.6	92.5	92.7
Turbid	92.5	93	14	16	92.7	92.7				
Dense			80	77.7						
Sediment	7.5	7	6	6.3	7.3	7.3	7	7.4	7.5	7.3

[124a] Owing to the impossibility of preparing 0.1 molar $Ca(OH)_2$, the equivalent amount of 0.02 molar solution was used.

On first mixing the latter series of tubes, that with 0.4 cc $Ca(OH)_2$ showed a dense suspension. On shaking again by hand just before placing in the shaking machine the 0.4 and 0.8 tubes showed dense suspension. After one hour on the machine the dense suspension had shifted to the 0.8 and 1.2 tubes. In other words, only a portion of the clay colloid was acted upon when first mixed, and 0.4 cc $Ca(OH)_2$ was sufficient to put it in suspension. When with further shaking more of the clay colloid was exposed to the action of the lime, a proportionately larger amount of lime was required to effect suspension. This behavior was frequently observed with other reagents and clays.

Barium Carbonate.—Barium carbonate within narrow limits is an energetic deflocculating agent. Its effect is apparently to stop the effect of calcium sulphate by completely precipitating it from solution: $BaCO_3 + CaSO_4 = BaSO_4 + CaCO_3$; or it may react with Na_2CO_3, which then exerts a deflocculating action. Lead acetate might be expected to give a similar reaction, but failed when tried with Prall Sagger clay.

ACIDIC DEFLOCCULANTS

Oxalic Acid.—Even oxalic acid may act as a deflocculant (Fig. 19), probably by reacting with some calcium salt.

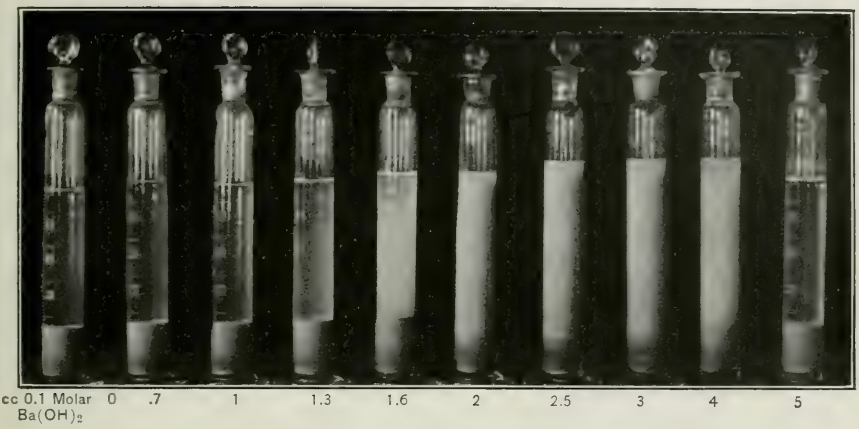

Fig. 17.—*Effect of additions of barium hydroxide to New Jersey sagger clay (No. 1, Jas. P. Prall, Woodbridge, N. J.)*

In each tube 5 grams clay; amount of $Ba(OH)_2$ as given above

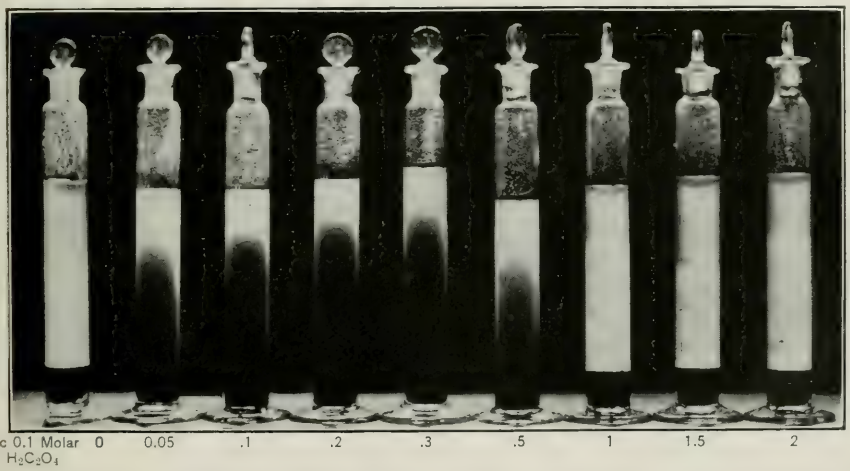

Fig. 19.—*Effect of additions of oxalic acid to a fire clay (No. 2, W. H. Wynn)*

In each tube 5 grams clay; amount of $H_2C_2O_4$ as given above

Tannic Acid.—Tannic acid appears to exert its deflocculant effect by taking into solution iron (or possibly aluminum) from colloid gels. It appears to be without action on clays not containing iron or aluminum, and deflocculates and is strongly colored by clays containing iron (Fig. 20). In the case of W. H. Wynn No. 1 fire clay the iron of the clay was wholly insoluble in water, but soluble in the tannic acid.

While the most probable cause of the deflocculating action of oxalic acid and of tannic acid is the removal of coagulating bases, yet that would leave equivalent amounts of hydrogen with the colloid matter. It seems possible, then, that certain free colloid

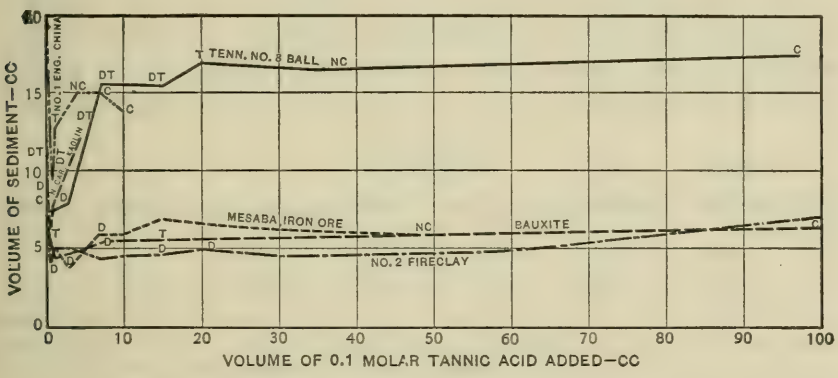

Fig. 20.—*Effect of additions of tannic acid to various clays, etc.*

Five grams substance; total volume 50 cc. Letters refer to the appearance of the supernatant liquid; C=clear, NC=nearly clear, T=turbid, DT=deeply turbid, D=dense.

acids within very narrow ranges are more soluble than the corresponding salts of the bivalent and trivalent metals.

DEFLOCCULATION BY HUMUS AND BY COLLOIDAL SUBSTANCES

Puchner [125] states that humus matter prevents the coagulation and sedimentation of a soil by salts, such as calcium chloride, even when the particles are large enough to be removable by filtration.

On the other hand, Dr. Chase Palmer, of the chemical laboratory of the United States Geological Survey at Washington, has informed the writer that he has found that the dissolution of silica in water in the presence of humus acids is merely accidental;

[125] Landw. Vers. Sta., 70, pp. 249–267; C. A., 3, p. 1566; 1909.

that the dissolution of each is caused by a slight alkalinity of the water. Moreover, he has coagulated silicic acid by organic acids of the same order of strength as the humus acids.

Colloidal substances may also deflocculate clays, the effect being probably similar in character to the effect of one colloid upon another. This question has been studied by Buxton and Rahe,[126] who found that two colloids will mutually dissolve or coagulate in a manner depending upon their specific nature and upon the proportions of each present.

DEFLOCCULATION BY DYESTUFFS

The deflocculation produced by dyestuffs is probably another case of the effect of one colloid upon another. A number of dyestuffs were tried, with 5-gram portions of J. Poole's No. 1 English china clay, with results which are presented in the following table:

TABLE X

J. Poole No. 1 English China Clay. Effect of addition of various coloring matters

(*a*) JANUS GREEN B (II MONAZO COLORING MATTER)[127]

Grams dye	0	0.01	0.02	0.03	0.04	0.14	0.24	0.34
Clear	29	34	34	34	.....	.....	.....	.....
Turbid	.....	.....	.....	.....	35	39	.....	.....
Dense	.....	.....	.....	.....	.....	.....	41	41
Sediment	21	16	16	16	15	11	9	9

(*b*) CONGO-RUBIN (III DISAZO COLORING MATTER).

Grams dye	0	.....	0.01	0.02	0.03	0.08
Clear	29	.....	[127a] 9	.....	.....	.....
Dense	.....	.....	[127b] 34	44	45	43
Sediment	21	.....	[127c] 7	6	5	7

[126] J. Med. Res., 20, pp. 113–136; 1909.

[127] Classification of Schultz and Julius's Organic Coloring Matters, 2d ed.

[127a] Pink.

[127b] Purple.

[127c] Blue.

TABLE X—Continued

(*c*) MALACHITE GREEN OXALATE[128] (X TRIPHENYLMETHANE COLORING MATTER)

Grams dye	0	0.01	0.02	0.04	0.06	0.11	0.16
Clear	29	[128a] 34	[128b] 28	20	21	27	28
Sediment	21	16	22	30	29	23	22

(*d*) METHYL ALKALI BLUE (X TRIPHENYLMETHANE COLORING MATTER)

Grams dye	0	0.01	0.02	0.03	0.04	0.09
Clear	29				10	
Turbid			3			
Dense		44	42	45	34	44
Sediment	21	5	5	5	5	6

(*e*) FAST ACID VIOLET R (XI XANTHENE COLORING MATTER)

Grams dye	0	0.01	0.02	0.03	0.04	0.05	0.06	0.08	0.13
Clear	29		4			12	3	3	
Turbid		40	37			32			
Dense				43	44		42	42	45
Sediment	21	10	9	7	6	5	5	5	5

(*f*) ACID ALIZARINE BLACK EXT. (XIII ANTHRACENE COLORING MATTER)

Grams dye	0	0.01	0.02	0.03	0.08	0.13	0.18
Clear	29	18				35?	34?
Turbid		22	([128c])	([128c])	([128c])	([128c])	([128c])
Dense			43	42	39		
Sediment	21	10	7	8	11	15	16

[128] Malachite green, although coagulating this and most other clays, deflocculates—e. g., a clay from Fort Pierre, S. Dak.—when the clay is in sufficient excess. A sufficient excess of dye to coagulate the clay is present in the test for estimating colloid content (p. 40). The unsuitability of many dyes for the colloid test is due to their deflocculating clays with the concentrations best suited for color comparisons.

[128a] Colorless.

[128b] Blue.

[128c] Opaque.

TABLE X—Continued

(*g*) METHYLENE BLUE DBB EXTRA CONC. (XVII THIAZINE COLORING MATTER)

Grams dye	0	0.01	0.02	0.045	0.095
Clear	29	[128a] 33	[128a] 32	31	[128b] 37
Sediment	21	17	18	19	13

(*h*) INDIGO CARMINE DRY (XXI INDIGO DERIVATIVE).

Grams dye	0	0.01	0.02	0.045	0.095
Clear	29	[128c] 39	38	[128b] 39	[128b] 39
Sediment	21	11	12	11	11

[128a] Colorless. [128b] Opaque. [128c] Dark blue.

16. COAGULANTS

The following reagents in these experiments acted invariably to coagulate the clays tested: Carbonic acid, H_2CO_3; potassium dichromate, K_2CrO_4; sodium acetate, $NaC_2H_3O_2$; hydrochloric acid, HCl; ammonium chloride, NH_4Cl; sodium chloride, NaCl; zinc chloride, $ZnCl_2$; magnesium chloride, $MgCl_2$; barium chloride, $BaCl_2$; calcium chloride, $CaCl_2$; ammonium nitrate, NH_4NO_3; sodium sulphate, Na_2SO_4; ammonium sulphate, $(NH_4)_2SO_4$; magnesium sulphate, $MgSO_4$; calcium sulphate, $CaSO_4$; ferrous sulphate, $FeSO_4$; ferric sulphate, $Fe_2(SO_4)_3$; lead acetate, $Pb(C_2H_3O_2)_2$.

Effect of Valence.—It is commonly understood that the precipitating power of metallic salts for negative colloids increases greatly in passing from a small valence to a larger,[120] e. g., NaCl to $CaCl_2$ to $AlCl_3$ to $SnCl_4$. However, on trying these four reagents with the sol obtained by water extraction of the Prall sagger clay, only $CaCl_2$ gave prompt precipitation, NaCl followed shortly after, $SnCl_4$ was hydrolyzed on standing over night and carried down the clay sol enmeshed, while $AlCl_3$ had no apparent effect. Here the clarification evidently depended on the specific solubilities of the reaction products of these salts and the clay used.

[120] U. S. Geol. Survey Bull. 388, p. 27; 1909. J. prakt. Chem., 25, pp. 431–452; 1882.

Jordis [130] also came to the conclusion that the precipitating power of valence depends on the insolubility of the products, those with high valence usually being most insoluble.

Coagulation by Freezing.—Coagulation is often brought about by freezing.[131] This is probably a salting out effect, due to concentration of salts in the mother liquor as the ice crystals separate out.

ADDITION OF SOAP TO CLAYS

The effect of soap upon ball and china clays is worthy of examination; the results are presented in Table XI and in part in Fig. 21.

TABLE XI

ADDITIONS OF ENGLISH "CROWN" SOFT SOAP TO 5 GRAMS J. POOLE'S NO. 1 ENGLISH CHINA CLAY

cc 1 per cent soap solution	0.1	0.3	1	3	10	30	98
Clear	81						
Turbid		78	81	84	83	2	93
Dense						93	
Sediment	19	22	19	16	17	5	7

ADDITIONS OF ENGLISH "CROWN" SOFT SOAP TO 5 GRAMS MANDLESANT CLAY CO. TENNESSEE BALL CLAY NO. 3

cc 1 per cent soap solution	0	0.5	1	3	5	7	10	15	25	48
Turbid	1	1	1	1	1	1	1	1	1	1
Dense	41	41	39	35	35	35	35	35	35	35
Sediment	8	8	10	14	14	14	14	14	14	14

The effects are of the same nature as those already discussed—with the china clays exchange of bases and sol formation; with the ball clay, salting out only. (See p. 111 for applications of this knowledge to cleansing processes.)

[130] Zs. Chem. Ind. Kolloide, **3**, p. 25; 1908.

[131] Zs. Chem. Ind. Kolloide, **3**, pp. 195, 196, 203. Müller: "Studien über die natürlichen Humusformen, p. 187; 1887. Landw. Versuchssta., **33**, p. 1; 1887; **58**, p. 187; 1903. Wohlny: Zersetzung der organischen Stoffe, p. 219; 1897. Landw. Jahrbücher, **12**, p. 222; 1883; **20**, p. 786; 1891; **21**, IV, p. 344; 1898. Mitt. der Landw. Inst. Univ. Breslau, **4**, p. 113; 1908. Forschungen a. d. Gebiet d. Agrikulturphysik **2**, p. 450; 1879.

18. EFFECT OF ADDITIONS OF SODIUM CARBONATE AND SODIUM SILICATE TO CLAYS

A few experiments on the effect of additions of sodium carbonate together with sodium silicate on the behavior of clays and clay mixtures were performed. The results are presented in the diagrams of Fig. 22, in which the contour lines show the volume of the sediment for additions up to 5 cc of 0.1 molar solutions of each of these reagents (cf. pp. 100-101).

As regards the behavior of clay in media other than water, very little work has been done, and little is known about it. Kerosene is commonly used in the Seger volumenometer by reason of its accepted freedom from action on the clay. It is stated by Hilgard [132] that the presence of alcohol or ether materially reduces the tendency to flocculation.

For purpose of comparison, the effect of additions of caustic soda and, in some cases, of hydrochloric acid to some other mineral substances was investigated, namely, to fuller's earth (Fig. 23); potter's "flint" (ground sand rock) (Fig. 24); feldspar (Fig. 25); mica (Fig. 26); iron ore (Fig. 27). The results obtained are apparent from the photographs reproduced in Figs. 23–27. Pure water seems to give the maximum effect with the ground sand rock and with the feldspar; this is doubtless due to their natural alkali content, which on addition of water forms an alkaline solution sufficiently concentrated to effect deflocculation.

Additions of sodium hydroxide were also made to bauxite and to air-dried peat, but produced only incomplete deflocculation.

III. APPLICATIONS

In the foregoing pages we have endeavored to show that the general behavior of clays is conditioned very largely by the possibility of a metathetical reaction between clay and reagent. The possibility of reaction is determined by the solubility relations of the possible solid phases (original substances and possible products) in the particular media. These relations are not known to us quantitatively, but we may, by reasoning from analogy and by inference from the phenomena observed, obtain some qualitative

[132] Am. J. Sci., 3, 17, p. 207; 1879.

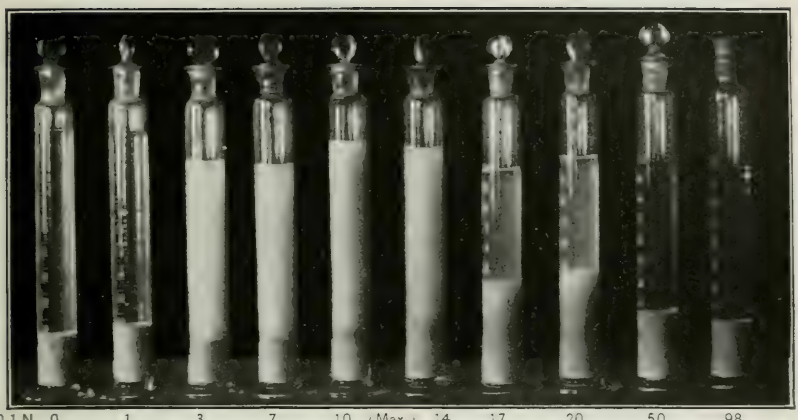

Fig. 23.—*Effect of additions of NaOH to Fuller's earth (Owl Commercial Co., Quincy, Fla.)*

In each tube 5 grams; amount of NaOH as given above. Maximum effect was observed with 10 cc 0.1 N NaOH

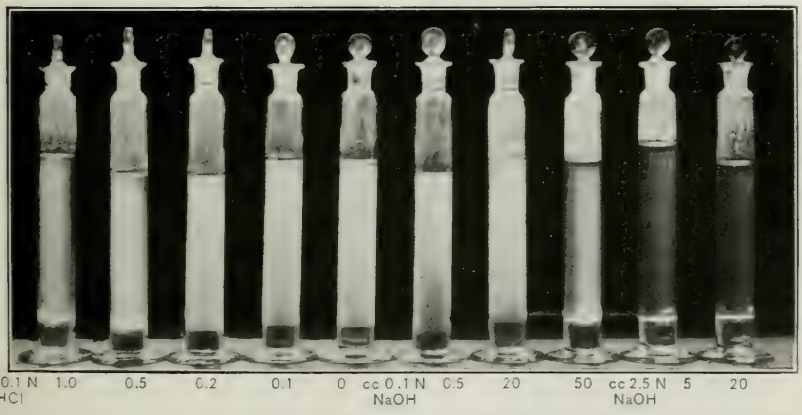

Fig. 24.—*Effect of additions of HCl and NaOH to quartz (dry-ground Pennsylvania "Sand Rock," Potter's Mining and Milling Co.)*

In each tube 5 grams; amount of reagent as given above

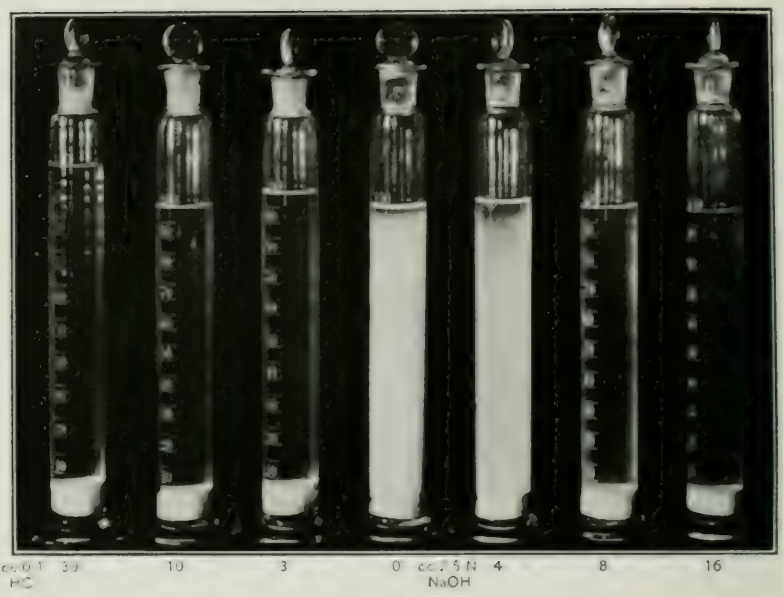

Fig. 25.—*Effect of additions of HCl and of NaOH to dry-ground orthoclase* (*Maine Feldspar Co., Auburn, Me.*)

In each tube 5 grams; amount of reagent as given above

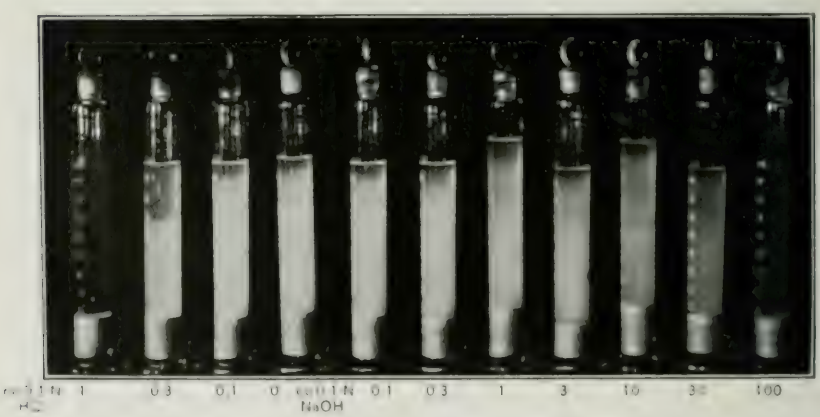

Fig. 26.—*Effect of additions of HCl and of NaOH to flake mica*

In each tube 5 grams; amount of reagent as given above

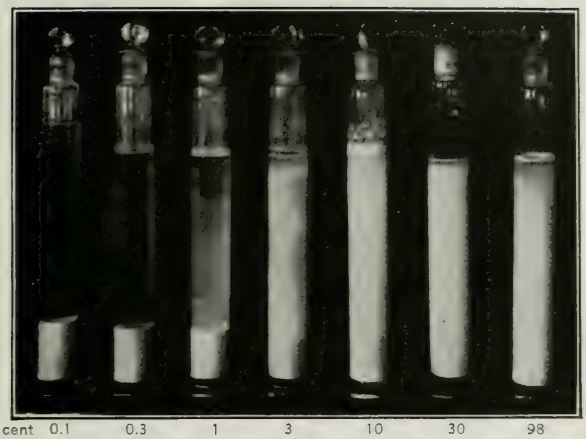

Fig. 21.—*Effect of additions of soft soap to an English china clay (No. 1, J. Poole)*

Cf. Table XI. In each tube 5 grams clay; amount of reagent as given above

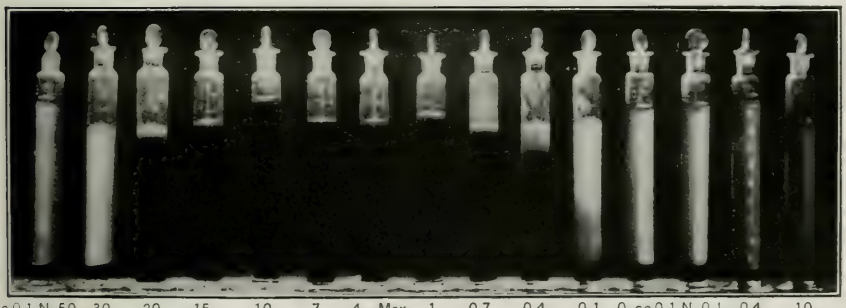

Fig. 27.—*Effect of additions of HCl and of NaOH to Mesaba iron ore*

In each tube 5 grams; amount of reagent as given above. Maximum effect occurred with ¼ cc 0.1 N NaOH

information with regard to these relative solubilities. This information can then be applied to the discussion and elucidation of

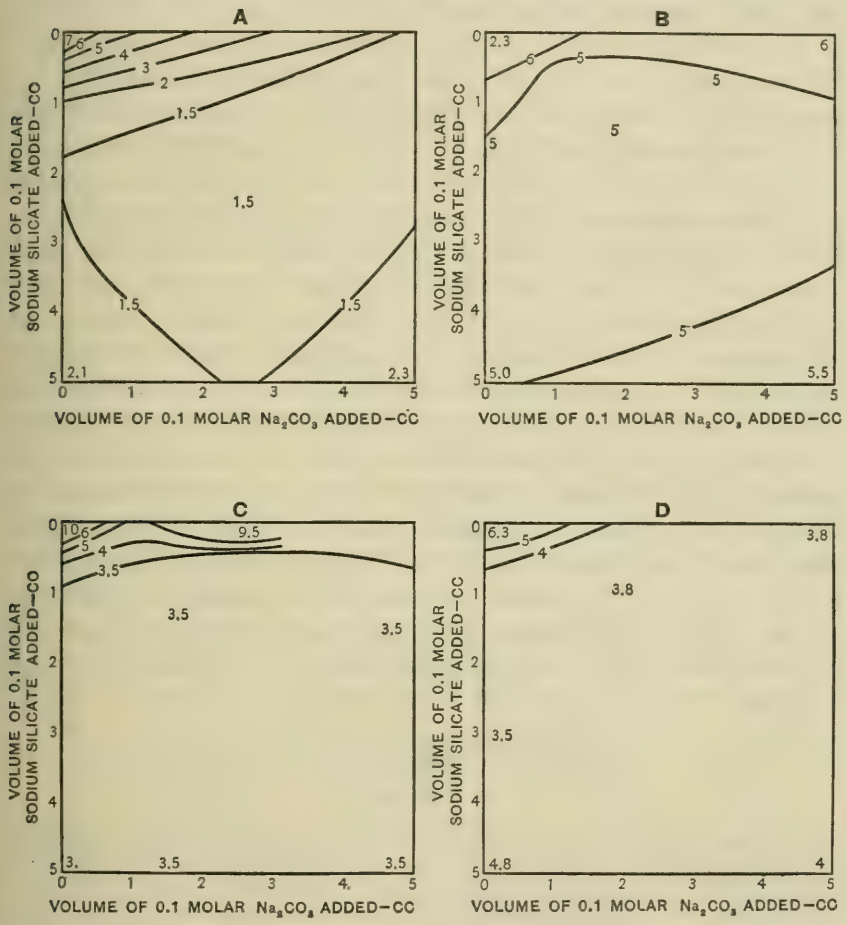

Fig. 22.—*Effect of simultaneous additions of sodium carbonate and sodium silicate to clays and to a body mix*

Amount of reagents as given above; total volume 100 cc. A, 5 grams Tennessee ball clay No. 3; B, 5 grams English china clay (No. 1 J. Poole); C, 2.5 grams Tennessee ball clay No. 3, 2.5 grams English china clay No. 1; D, 1.25 grams Tennessee ball clay No. 3, 1.25 grams English china clay No. 1, 0.5 grams potash felspar, 2.0 grams quartz. The numbers inside the diagrams represent the volume (in cc) of the sediment; the "contour" lines are drawn through the points at which equal volumes of sediment were observed.

specific problems. The purpose of this section is to make a few such applications.

Before proceeding to the specific applications we desire to mention a few points with regard to the general question of the regulation and improvement of clays.

By making series of tube experiments, similar to those described in this paper, it would seem to be practicable to determine quantitatively the effect of any reagent upon a clay and to make direct use of such knowledge in the pottery. Such knowledge would be, of course, independent of any theory; but, we believe, that the principles made use of in this paper would be of great aid in correlating the phenomena, and hence in enabling us to predict what would happen in particular cases. Moreover, it would seem that systematic research work of this character would be of great advantage to the industry. For instance, such work should enable one to ascertain the most desirable state of a clay for each specific purpose and to transform it into that state. If, for example, it should be found that an acid gel, free from soluble salts, is most desirable, it would be a simple matter to blunge up the clay with a little acid and to wash several times thereafter with water, each time decanting off the liquid after the clay had settled. This process would remove the bases combined with the gel, as well as the soluble salts in the clay. Moreover, it would improve the color of clays carrying iron. In a similar way any base might be introduced if found desirable.

A. IMPROVEMENT OF CLAYS

1. WEATHERING

It is well known that certain fire clays and shales are improved by the process of weathering.[133] The colloid matter of such clays is probably in a condition similar to a dry sponge in regard to its ability to take up water; so that the weathering increases plasticity by promoting a thorough penetration of water. The process is promoted by drying out in summer, which, by coagulating any sol and by partially setting some of the gels, increases the porosity of the mass and the ease of penetration for subsequent additions of water. Weathering is also promoted by freezing in winter. First, by heaving the grains farther apart and, second, by con-

[133] U. S. Geol. Survey Bull., 388, p. 13, 14; 1909; Bull. 330, pp. 467, 1908.

centrating the soluble salts in the mother liquor from which the ice crystals separate, and so causing any clay sol to be coagulated. Both of these actions facilitate the subsequent movements of water through the clay.

Weathering may, however, proceed too far. The writer knows of a case where fresh-mined shale made a paving brick giving a rattler test better by 2 or 3 per cent than brick made from the same shale after it had weathered two or three months. The swelled sponge of the weathered clay did not burn to as dense a product as the fresh-mined unexpanded clay. In an opposite [134] case the absorption of moisture from the damp air of a drier caused the block of unweathered fire clay to expand and crack.

Another action taking place at the same time is the removal of soluble salts by the rain or hose water applied to the pile of weathering clay. We know absolutely nothing as to whether the working properties of the clay and the strength of the product are injured or improved by this removal of salts. We do know that salts liable to cause scum are removed, but whether these salts are otherwise desirable and which, if any, is most beneficial is an uninvestigated question. Langenbeck [135] says:

> Those who form their ware freehand on the potter's wheel insist that a clay loses much of its plasticity in washing, becoming "punky"—that is, elastic rather than plastic.

Too much pugging or wedging is also said to cause punkiness.

2. EFFECT OF SALTS CONTAINED IN SLIP-HOUSE WATER

The soluble salts in slip-house water may have very important effects. The blunging of clay is slower in hard water than in pure water; addition of suitable alkali would undoubtedly hasten the blunging, but would at the same time lessen the plasticity of the clay.

The specific nature of the salts may make special difficulties. It is well known that sulphates, whether derived from the clay or from the slip-house water, tend to collect at the edges of pottery ware, causing "dry edges," on which the decoration is dulled or wholly spoiled. It would seem that the potter, as well as the brick-maker, could with advantage use barium carbonate in his mix to

[134] Trans. Am. Cer. Soc., 11, pp. 385, 390, 1909.

[135] Chemistry of Pottery, p. 79, 1895.

overcome the difficulties caused by sulphates. Seger [136] therefore proposed that barium carbonate be added to pottery mixes to precipitate the sulphates that cause dry edges, etc.; this is stated by Joshua Poole to be a frequent practice in the Staffordshire district.

If the slip-house water takes up salts from the clays rather than adds them, they by throwing away all the filter-press water, the quantity of soluble salts in the clays can be reduced.

When one of our largest potteries commenced operations it used exactly the same materials (usually from divided shipments) and the same body formula as another plant which was then successfully operating. But there was complaint in the clay shop of loss of ware. The help claimed that the body was not as plastic as at the old plant. This condition lasted for some months, and gradually was lost sight of. Now, the clay bins were made of concrete, and there was some seepage of ground water inward. The blungers were lined with brick, laid in cement. The troughs from blunger to agitator and from sifter to agitator were of cement. The agitators were lined with cement. After some months' running the bottoms of the agitators were so worn that it was necessary to reline them. In all of these places, then, the clays could take up free lime from the cement. This investigation has shown that under certain conditions lime may be an effective deflocculating agent (p. 69, Fig. 18); apparently it was responsible for the trouble. If such is the case, then in another such instance it would be easy to add acetic acid or vinegar in sufficient amount to overcome the trouble wholly and with no disadvantageous effects.

Seger,[137] however, added 0.1 per cent of calcium oxide to a porcelain body to prevent efflorescence of iron salts and said it was without ill effect on the clay; the reason being that it was probably completely neutralized in precipitating the iron salt.

Before leaving this question it may be said that we are as yet ignorant of the effect of varying the base in combination with the gel; as to whether, for instance, the H gel is superior to an alka-

[136] Collected Writings. Am. Cer. Soc. Translation, pp. 649, 1148, 1902. Langenbeck: Chemistry of Pottery, pp. [illegible].

[137] Collected Writings. Am. Cer. Soc. Translation, p. 1149, 1902.

line-earth gel or vice versa. It is, however, generally accepted that a clay becomes most plastic when it sours or becomes acid on ageing;[138] this evidence, nevertheless, would not of itself justify the statement that H gels are to be preferred.

Simcoe and Smith [139] made experiments in which they varied the relative amounts of "plastics" and "nonplastics" in dust-pressed wares. They found no great difficulty with a body composed entirely of ball clay, but had to add gum tragacanth to tender bodies.

3. TREATING EXCESSIVELY COLLOIDAL CLAYS

On the other hand, a clay may be too plastic to work satisfactorily; so that, if it is to be worked at all, some method of reducing its colloid content must be employed.

To accomplish this purpose, Bleininger [140] has investigated a method of heating excessively colloidal clays before use in the brick machine, so as partly to destroy their ability to take up so much water. It consists in heating the clays to a temperature of 250° to 300° C., a process which is accompanied by decided increases in the specific gravity of the clay and by a "setting" of the colloidal material. The "setting" is perfectly analogous to the changes produced in other colloids by heating and referred to earlier (p. 38); it consists of a shrinking together of the colloidal particles as they lose water, with the formation of harder and larger particles, which are then attacked by water with comparative slowness. Hence, the plasticity of a clay is reduced by the process of preheating, except it be allowed to remain again in contact with water for a comparatively long time.

The temperature used is chosen so that sufficient unaltered colloidal material is left for plasticity.

Terry [141] said that in drying china clay on fire-brick flues previous to shipment "The temperature should never be allowed to rise so high that the workmen can not walk on the tiles, otherwise the clay may become baked and damaged."

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[138] Seger: Collected Writings, p. 722, 1902.

[139] Trans. Am. Cer. Soc., 12, pp. 196–204, 1910.

[140] Trans. Am. Cer. Soc., 11, pp. 392–406; 1909; 12, pp. 504–516; 1910; and especially Bull. Bureau of Standards, 7, pp. 143–196; 1911, where the subject of preheating of clays is fully discussed.

[141] Pigments, p. 176; 1893.

It seems probable that in some cases the addition of a suitable reagent would dissolve the excess of the colloidal constituent, making a sort of thick solution to replace the ordinary tempering water, and also giving a denser product of higher crushing strength. Such a product might require unusual care in drying.

It would be desirable to ascertain if addition of acid would improve the working qualities of the alkaline clays often found in arid regions.[142]

4. USE OF COLLOID ADDITIONS

It has been the custom for many years to make colloidal additions to clay bodies, especially in pottery work; such as gelatine, glue, starch, gum arabic, dextrin, milk, and silicate of soda.[143] They are generally added to assist the cementing properties of a slip (such as the slip used in sticking handles on cups), or in some cases to diminish the amount of water required (silicate of soda, tannin).

In India[144] many additions are made to the local clays used for pottery. Among these are cow dung, leaves, horse dung, mule dung, rotten paper, gum, and starch. Some of the additions probably are valued more for their mechanical properties than for their colloid properties, as in the following cases: 29 g cotton wool to 1 kg clay; also 0.5 kg babul tree gum, 1 kg belgiri, 0.5 kg brown paper, 0.5 kg old cotton wool to 1 kg common black clay (this product is used for making unburned toys).

Simcoe and Smith[145] say:

> Many potters have for years used some sort of gum in their body, mixing in the blunger about a quart of a starchy mass to 3,000 pounds of body. * * * Bourry[146] also speaks of the use of gums under the head of "Agglomerative and agglutinative material," specifying the use of glue, gum, lichen, dextrin, soap, sugar, and molasses, and for ordinary ware, tar. He further states that they use black soap and parchment glue in the soft French porcelain. * * * We do not put our scraps back into the blunger. * * * It is a common experience with every plastic clay, or clay having gum in it, that you get into trouble with the filter press.

They also found the addition of kerosene and lard oil, mixed 3:1, to assist the clay to free itself from the molds, and with no injurious effect on plasticity.

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[142] Seger: Collected Writings, Am. Cer. Soc. Translation: p. 722.
[143] U. S. Geol Survey Bull. 388, p. 12; 1909. Kerl-Cramer-Hecht, pp. 1513, 1514, 1515; 1907.
[144] Pottery Gazette, 35, pp. 1158–1160; October, 1910.
[145] Trans. Am. Cer. Soc., 12, p. 199; 1910.
[146] Treatise on Ceramic Industries, p. 70; 1901.

Bourry further mentions grease, milk, and an emulsion of casein in boric acid.[147]

Gum tragacanth and starch are used in making porcelain teeth.[148]

Zimmer [149] has given a good example of the proper method of adding colloidal material to a clay. He mixed the clay slip with silicate of soda, which, because of the soluble nature of the addition, gives a most uniform and intimate penetration. Then he added sufficient hydrochloric acid to react with all the alkali of the silicate of soda and coagulate the silica from it as gel. The excess of acid and sodium chloride was then washed out. This gave a plastic clay of unusually high shrinkage, and improved the color. A similar amount of silicic acid prepared separately, air dried (but containing 43 per cent H_2O), when added to the same clay, made it very short and hardly workable.

A failure to secure sufficiently intimate mixture may account in part for the unsatisfactory results obtained by Grout [150] after adding colloidal alumina or silica to clays.

Acheson [151] reports both deflocculation and improved plasticity from the use of tannin with clays, the effect depending, of course, on the quantity of tannin used and on the nature of the clay. Some of those who have tried to verify his results have encountered twisting and warping of ware, and so have condemned them. This lack of success may, however, be due to an imperfect incorporation of the reagent with the clay.

It would seem as if faults due to imperfect mixing led Keppeler[152] to his patented process of improving clays. This consists, first, in deflocculating by alkali; second, making an addition of colloidal material from humus; third, reprecipitating all together by adding acid.

Auclair [153] has patented the preparation of a pure crystalline ceramic paste by dissolving out the colloids with alkali and

[147] Treatise on Ceramic Industries, p. 738.

[148] John Q. Byram: Principles and Practice of Filling Teeth. New York: Consolidated Dental Mfg. Co., p. 13; 1908. George Evans: A Practical Treatise on Artificial Crown-Bridge and Porcelain Work. Philadelphia: S. S. White Dental Mfg. Co., 7th ed., p. 343; 1905.

[149] Trans. Am. Cer. Soc., **3**, pp. 30–32; 1901.

[150] West Va. Geol. Survey, **3**, pp. 47, 49, 1906.

[151] Trans. Am. Cer. Soc., **6**, p. 31, 1904. British Patent No. 7776, Apr. 3, 1907.

[152] Z. angew. Chem., **22**, p. 526, 1909. German Patent No. 201987, Aug. 4, 1906. Chem. Abstracts, **3**, p. 494, 1909.

[153] French Patent No. 372858, Dec. 22, 1906: Chem. Abstracts, 2, p. 2436, 1908.

removing the sol by filter pressing. Recently the writer[154] gave reasons for thinking that the colloidal material of kaolin has greater shrinkage than that of ball clays. It seems likely that a safer body mixture could be made if all the colloid matter were derived from the ball clay. Hence there seems good reason for the patent for removing colloids from kaolin. The principal objection to the use of ball clays is that they carry much dirt, mainly granules of iron minerals. It would seem to be feasible to dissolve out by suitable reagents the colloidal material of ball clays, leaving a residue containing most, if not all, of the discolorants. The colloid could be coagulated by acid when required, and could be very uniformly incorporated with other materials; for instance, with the crystalline kaolin mentioned above. Of course, these would be expensive processes; but the demands upon the ceramic industry for high-grade products are daily becoming more exacting, and for some purposes nothing is too good.

Use of Slip Kiln Increases Colloid Content.—It is well known that boiling a clay with water for even a very short time decreases the content of crystalline quartz and kaolinite and increases the proportion of colloids. Thus Hilgard[155] said that boiling serves "to reduce the kaolinite ingredient of soils and clays to the amorphous plastic, diffusible modification. As to boiling, I have succeeded in rendering diffusible and very plastic the 75 per cent of clayey ingredient in a white, chalky pipe clay, resembling kaolin, and which naturally is but very slightly plastic, by boiling for about 85 hours."

In agreement with this, L. Solon[156] stated that "the materials employed for making soft porcelain in France in the early days were more plastic than when boiling was abandoned as a useless complication." C. F. Binns[157] has said practically the same thing in regard to the replacement of the slip kiln in England by the filter press for bone china.

If, however, the clays being dried by fire should become overheated beyond the boiling point of water the setting (or coking) of the gels would lead to a loss of plasticity. Such appears to have been a common experience in Germany.[158]

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[154] Trans. Am. Cer. Soc., 11, p. 550, 1909. U. S. Geol. Survey Bull., 388, p. 53, 1909.
[155] Am. J. Sci., (3) 17, p. 211, 1879.
[156] Pottery Gazette, p. 1293 (Nov. 1, 1907). Trans. Eng. Ceram. Soc., 5, p. 72, 1905.
[157] Trans. Am. Cer. Soc., 12, p. 177, 1910.
[158] Kerl-Cramer-Hecht, p. 269, 1907.

5. INCREASE OR DECREASE OF REFRACTORINESS

Clays may presumably be rendered less fusible by treating them with soluble salts of such character that—by means of the exchange of bases—the bases entering form compounds melting at a higher temperature than those originally present.[159] Conversely, pottery clays may be made to mature at a lower temperature by removing the more refractory bases by treatment with solutions of alkali salts, e. g., common salt, potassium nitrate, etc.[160]

6. SOLUBLE COBALT STAINS

The simple addition of cobalt as chloride, sulphate, or nitrate to stain a clay ware is not practicable, for the writer has found that only about half of it is taken up by the clay, the rest remaining with the filter press water. As cobalt salts are rather expensive, this loss could not be viewed with complacency. Moreover cast ware could not be made with a body so colored, for in drying the cobalt would effloresce at the edges and so color them more deeply than the rest. It is necessary, therefore, to precipitate the cobalt compound with an alkali (NaOH, KOH, Na_2CO_3, but not NH_4OH) just before using, or to use it as a ground frit. Such soluble cobalt additions are in practice made to earthenware bodies containing calcium carbonate, but the precipitation as carbonate is incomplete and unsatisfactory.[161]

7. PURIFYING KAOLIN

In the preparation of china clay for the market the crude clay is made up into a slip with water, and the coarse rock débris, mica, etc., removed by settlement in troughs or by sifting. The clay is then concentrated by filter pressing or by sedimentation, followed in either case by drying. It is a more or less common practice to accelerate the sedimentation by adding alum[162] to the slip. As from 30 to 50 per cent water is to be removed by the "dry," it is evident that a certain amount of undesirable sulphates is included in such cases.

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[159] See also Kerl-Cramer-Hecht., p. 175, 1907.

[160] Ibid., p. 195.

[161] Kerl-Cramer-Hecht., pp. 1140, 1141, 1907.

[162] Alum or ammonium carbonate: Sprechsaal, p. 244; 1904. Alum, Ries: Clays of the U. S. East of the Mississippi River, p. 35; 1903.

For paper clays, one of the commercial requirements is a white color in the raw condition; hence it is desirable that certain organic matters of red or yellow tint be removed or bleached. For whiteware clays it is essential that dark burning iron compounds should be removed from the raw clay. A. G. Salamon and several associates have covered both these cases in a series of patents, in each of which the clay is treated with some reagent, filter pressed, and then the excess of the reagent washed out on the filter press. The patents are as follows:

British patent, 13179 (June 20, 1908). "A weak solution of alum, or of sulphate of alumina, or, sometimes, sulphuric acid."

British patent, 21260 (Oct. 8, 1908). Chlorine water and a little sulphuric acid.

British patent, 2294 (Jan. 30, 1909). Oxalic acid at 55°.

British patent, 2295 (Jan. 30, 1909). Sulphurous acid or a suitable sulphite, bisulphite, or other compound of sulphurous acid which is capable of combining with the coloring matter and forming soluble salts or compounds.

Karl Langenbeck[163] decolorizes kaolin, etc., containing iron, by subjecting it to hydrogen sulphide to form ferrous sulphide, which is then removed by oxidation and lixiviation.

B. MECHANICAL ANALYSIS OF CLAYS

Mechanical analysis is a name given to the operation by which the clay is separated into groups of grains of different sizes, the amount of each size being weighed. The coarser sizes are separated by taking advantage of the different rates at which they fall in water, the finest being the slowest to settle. The mechanical analysis of paving brick shales is very important; for, in a general way, the finest grained paving brick shales make the weakest brick. The finest grained pottery clays have the biggest loss in the kilns.

The data obtained make possible a criticism of present methods of conducting the mechanical analysis of clays.

[163] U. S. Pat., 893595.

8. PREPARATION OF CLAYS FOR MECHANICAL ANALYSIS

Shaking with cold distilled water in sufficient quantity will deflocculate a clay perfectly if all its colloid matter is in the form of soluble alkaline compounds, but otherwise not. If more water is used than the quantity that just suffices, the crystal matter will be attacked and tend also to go over to the colloid form. If hot water is used, or if grinding is resorted to, the above actions will be greatly accelerated.

The use of hard water will tend to keep the colloid matter coagulated on the crystal grains.[164] In elutriations with incompletely deflocculated clay there is a tendency to ball up and to adhere to the walls of the apparatus,[165] which is wholly absent with perfect deflocculation. Also the fractions of incompletely deflocculated clay on drying shrink, crack, and roll up, none of which is the case with wholly granular residues; such shrinkage is, of course, a direct consequence of the presence of collodial material in the fractions.

Kashinskii[166] compared the efficacy of shaking and boiling as means of deflocculation; and found that by long-continued shaking one obtains, in general, fewer particles less than 0.01 mm, and a greater number of particles of 0.25–0.05 mm, than by boiling; this difference is equalized to some extent if the shaking is carried on with large quantities of water.

9. EXTRACTION WITH ACID, WATER, AND AMMONIA

The method of Schloesing[167] is the most generally applicable of the methods in use. He extracts the clay with a portion of nitric or hydrochloric acid and then washes till the filtrate is no longer acid; this removes the soluble salts and most of the basic ions of the gels. He then treats with ammonia, in proper proportion, which forms the ammonia sol of the colloids and leaves the crystals bare.

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[164] Sachse and Becker: Landw. Vers., **43**, p. 15; 1894. Z. Chem. Ind. Kolloide, **3**, p. 198; 1908.

[165] Kerl-Cramer-Hecht: p. 79; 1907. Hilgard: Am. J. Sci., (3) **17**, pp. 205–214; 1879. Wiley: Agricultural Analysis, I, p. 209; 1894. Seger: Collected Writings, Am. Cer. Soc. Translation, p. 1110; 1902.

[166] J. Exp. Landw., **9**, pp. 188–194; Chem. Abstracts, **3**, p. 2601; 1909.

[167] Compt. rend., **136**, p. 1629; 1903; **137**, p. 369.

J. Dumont[168] has a suggestive, but less general, scheme. The sample of soil, after treatment with a 60 per cent calcium nitrate solution to float off vegetable water, is boiled for at least one hour in 4 per cent oxalic acid, filtered, washed with nitric acid to remove calcium oxalate, and subsequently with distilled water, after which it is digested for 1 or 2 days with 20 per cent ammonia. It is then centrifuged at 1000 r. p. m. to remove sand, settled 24 hours to give loam, treated with ammonium carbonate to precipitate the clay, and then with hydrochloric acid (or is evaporated) to obtain the humus. The sands are centrifuged 10 minutes with Thoulet liquid (potassium mercuric iodide, sp. gr. 2.8) to remove ferromagnesian minerals, then with liquids of smaller specific gravity to separate quartz, orthoclase, and mica. His methods appear to be rather drastic for the best results.

10. EXTRACTION WITH AMMONIA

The Bureau of Soils[169] of the United States Department of Agriculture take 5 grams clay, 75 cc water, add 10 drops strong ammonia, and shake violently for 6 hours. The shaking is much in excess of what would be required with a proper choice and manipulation of solvents. The ammonia is found by them to be useless on soils containing carbonates, and is omitted with such soils. Its action in such cases is to assist in salting out the colloids rather than to assist in dissolving them. Ammonia will be found most effective with acid soils low in soluble salt content. It forms the ammonia sol from these and thus uncovers the grains, except it be prevented by the salting out effect of the soluble salts present or of excess of the reagent.

11. EXTRACTION WITH SODIUM HYDROXIDE

The Tonindustrie Kalender recommends 1 cc sodium hydroxide solution (strength?) to 40 grams of clay. This is a more vigorous reagent than ammonia, and so can overcome more soluble salts. On the other hand, if the clay is alkaline, it will assist the more vigorously in salting out the colloids, and so hinder deflocculation.

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[168] The Mineralogical Analysis of Arable Soils: Compt. rend., 140, 1111; 1905. Enveloping Films of Soil Grains: Compt. rend., 149, 1287; 1910.

[169] Bureau of Soils, Bull. 24, 9, 20; 1904.

Best Proportion of Alkali.—In general, alkalies are efficient for removing the colloid coating from the grains when, first, the clay is not already alkaline, second, soluble salts are low, third, the colloid is not combined with polyvalent bases, such as calcium, magnesium, iron, or aluminum; fourth, just the right amount of alkali, as determined by tube experiments, is used.

It is exceedingly important that a slight excess of alkali shall not be added. In Fig. 2, which shows the effect of sodium hydroxide on the New Jersey sagger clay of Jas. P. Prall, it will be noticed that about 3 cc 0.1 *N* NaOH reduces the bulk of sediment to 3 cc. This sediment presents a clean, granular appearance. With this quantity the sol in the tube above the sediment has reached its maximum density; up to 37.5 cc may be added without producing any further change in appearance. With further additions, a gradual stiffening of the gel seems to set in, accompanied by a diminution of its volume and an increased carrying power. As it takes up first the finest part of the sediment, then the coarser portions, the sediment appears to diminish, to become less distinct, and finally to become identical with the coagulated gel. Obviously while the colloid matter is able to buoy up the granular matter of the clay it is in a very unsuitable condition for the mechanical analysis.

12. USE OF ALKALINE PRECIPITANTS

We do not know if anyone else has used alkaline precipitants to deflocculate clays for mechanical analysis, but we find them very efficient where the gel is combined with polyvalent bases or the soluble salts contain polyvalent bases. We have used sodium oxalate mostly, but potassium and ammonium oxalate seem to be nearly as efficient. In special cases, other reagents might be especially adapted to remove the compounds present; but any reagent giving perfect deflocculation should be satisfactory.

C. METHODS OF MECHANICAL ANALYSIS

Sedimentation and Elutriation.—The two general methods of mechanical analysis are sedimentation and elutriation; the former requires the more skilled operator and frequent standardization of the sizes of grain. The principal difference between the two

is that the former is intermittent, while the latter is continuous and usually employs a much larger volume of water. It is well established that water exerts a solvent effect upon minerals, and that this effect is greater the higher the temperature. Hence, it is desirable that, in mechanical analysis, the volume of water used and its temperature be kept as low as possible. This consideration is a strong argument for discarding elutriation methods and adopting sedimentation. It seems probable that instead of running elutriations until the overflow is clear, they should be run only for a definite length of time. Further, when ordinary tap water is used in elutriation, a great volume is required; consequently there is liability that the bases in it will undo the work of the deflocculating agent. This has happened when sodium oxalate had been used with the clay.

This difficulty may be obviated by combining sedimentation and elutriation, as follows: The greater part of the sol may be removed by sedimentation and decantation four times repeated, using distilled water and removing 90 per cent of the liquid each time; then the granular residue may be elutriated with tap water. In such a case, where 30 minutes were allowed for each sedimentation, it was found that 0.3 per cent crystalline matter was lost which ought to have remained in the third can.

An alternative method is to decant into the third can,[170] to wash the sediment into the first can, and to fill the second can with distilled water; and then elutriate with tap water. Most of the sol will then have overflowed from the third can before the tap water reaches it.

Another difficulty noticed in elutriations with metal cans is a tendency for fine clay that should overflow to lodge on the conical bottom and the vertical sides. This is due to a partial corrosion of the metal of the can and can not be obviated by using a sharper cone. It was evidently observed by Parmelee and Moore [171] in their comparative study of methods of mechanical analysis, for in one of their experiments they had the inside of the cans varnished.

[170] Trans. Am. Cer. Soc., 6, p. 185, 1904. S, p. 345, 1906, 11, pp. 469, 489; 1909. Proc. Engrs. Soc. West Pa., 25, p. [illegible], 1909.

[171] Trans. Am. Cer. Soc., 11, p. 477; 1909.

Sedimentation methods include those where gravitation is the force causing the grains to collect at the bottom of the vessel, and those where centrifugal force causes a much more rapid collection. Owing to the packing action of the centrifugal machine, the liquid overlying the grains is easily decanted, while a disturbance of the loose-lying grains in a sedimentation experiment is best avoided by siphoning off the water. The centrifugal soil elutriator of Yoder [172] is apparently impracticable as the sediment packs in so as to stop the flow; it is really a sedimentation apparatus.

It is desirable to study whether slightly alkaline water will give better results than pure water in making the successive changes; also whether there is a limit to the number of changes of water that should be employed (to minimize the solvent effect upon crystal grains). Accordingly, a number of experiments were undertaken, the results of which are brought together in the following table. In each case the amount of reagent used was the minimum amount required for complete deflocculation, except where several proportions of one reagent were tried.

It is thought that in some of the runs with the Tennessee No. 3 ball clay too much alkali was used.

It should be said that the experiments were made before the ideas announced in this paper were fully developed.

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[172] Utah Expt. Sta., Bull. 89, p. 16; 1904. Out of print.

TABLE XII

Effect of Method of Preparation on Comparative Elutriations with the Schultze Apparatus

Clay	Reagent added to 50 g clay	Can 1, 0.05773*	Can 2, 0.03543*	Can 3, 0.01671*	Overflow, 0.0050*	Remarks
Maine Feldspar Co., orthoclase	Tap water, boiled	4.7	22.3	22.3	50.7	
	Distilled water, cold	13.14	29.64	7.98	49.24	
Harris Clay Co., North Carolina: Kaolin	Tap water, boiled	0.10	7.08	31.64	61.18	Overflow turbid for 48 hours
Same sample, dyed with malachite green	Tap water, boiled	1.12	6.04	77.58	15.26	
	30 cc 0.1 *N* $Na_2C_2O_4$	2.38	29.04	10.28	58.30	Do.
	10 cc 2.5 *N* NaOH	2.14	27.62	10.30	59.94	Do.
		2.68	27.94	10.56	58.78	Do.
Hall Clay Co., Georgia, kaolin	Tap water, boiled	1.80	1.08	11.84	85.28	
	10 cc 0.1 *N* NaOH	1.96	9.76	6.02	82.26	
J. Poole, No. 1 English china clay	Tap water, boiled	0.2	nil	16.9	82.8	
	30 cc 0.1 *N* NaOH	0.4	10.86	9.48	79.62	
Knowles, No. 15 English china clay	Tap water, boiled	0.1	0.9	24.6	74.4	
	30 cc 0.1 *N* NaOH	0.22	14.64	9.82	74.98	
Hamill & Gillespie, A1 English china clay	Tap water, boiled	.....	.....	17.4	82.6	
	2 cc 2.5 *N* NaOH	0.08	10.82	9.08	80.02	
Atlanta M. & C. Co., Georgia, washed kaolin	Tap water, boiled	3.60	9.26	17.98	69.16	
	50 cc 0.2 *N* $Na_2C_2O_4$	2.06	6.92	4.36	86.65	
Edgar Plastic Kaolin Co., Florida, kaolin (dyed)	Tap water, boiled	1.7	48.5	20.4	29.4	
	20 cc 0.1 *N* NaOH	0.46	4.36	4.67	90.51	
	6 cc 2.5 *N* NaOH	0.16	3.34	6.44	90.06	
Knowles, No. 12 English, ball	Tap water, boiled	8.64	4.88	3.9	82.6	
	8 cc 2.5 *N* NaOH	2.82	2.22	0.66	94.30	
	100 cc 0.2 *N* $Na_2C_2O_4$	11.52	4.32	0.80	83.36	First can largely coarse stuff that screens would catch
Johnson-Porter C. Co., Tennessee, ball No. 9	Tap water, boiled	3.08	3.74	12.76	80.42	
	8 cc 2.5 *N* NaOH	1.82	3.50	0.98	93.70	Apparently cleaner than $Na_2C_2O_4$
	100 cc 0.2 *N* $Na_2C_2O_4$	2.50	5.46	1.32	90.72	
Mandle-Sant C. Co., Tennessee, ball No. 3	Tap water, boiled	9.24	3.64	8.84	78.28	Residue caked
	140 cc 0.1 *N* NH_4OH	0.74	0.90	1.88	96.48	
	90 cc 0.1 *N* NH_4OH	0.16	0.48	1.59	97.77	
	50 cc 0.1 *N* NaOH	0.21	0.16	0.83	98.81	Best value
	150 cc 0.1 *N* NaOH	0.01	0.31	0.92	98.76	
	80 cc 0.1 *N* NaOH;	0.02	0.24	0.43	99.31	

*These numbers represent the average diameter (in mm) of the particles.

TABLE XII—Continued

Clay	Reagent added to 50 g clay	Can 1, 0.05773	Can 2, 0.03543	Can 3, 0.01671	Overflow, 0.0050	Remarks
Jas. P. Prall, New Jersey, No. 1 light sagger	Tap water, boiled..	2.56	3.30	15.24	78.90	Third can caked
	Distilled water, boiled	5.62	18.78	6.84	68.76	All 3 cans caked
	Boiled, then dropped in 1 liter 0.1 *N* NaOH while running	3.85	7.96	1.93	86.26	Residues not caked
Diamond Clay Co., Ohio, fire clay	Tap water, boiled..	65.98	5.50	5.90	22.62	61.64 per cent on 120 mesh. 4.34 per cent in first can
	50 cc 0.2 *N* $Na_2C_2O_4$.	42.70	13.96	4.68	38.66	29.46 per cent on 120 mesh. 13.24 per cent in first can. Each grain microscopically homogenous but compound
	Same, boiled 5 minutes in 200 cc liquid	29.58	10.94	3.58	55.90	19.60 per cent on 120 mesh. 9.98 per cent in first can. Appears the same as above
	Same, boiled 10 minutes in 400 cc liquid	32.73	14.30	1.74	51.23	12.23 per cent on 120 mesh. 18.30 per cent in first can
Joint clay, Champaign, Ill. (normal)	80 cc 0.1 *N* NaOH..	6.70	26.56	5.07	61.66	
Same (preheated to 300°)	.....do.....	30.12	37.25	4.39	28.23	Set gel in can residues

The preceding table compares results obtained on the one hand by boiling (1 or 2 minutes) with hard tap water, then shaking mechanically at least an hour, and, on the other hand, by treating cold with a deflocculating agent, then shaking mechanically for an hour. Boiling decreases the size of grain in the first and second cans with feldspar and with the purer kaolins (Harris, Hall, Poole, Knowles, and Hammill and Gillespie). Microscopic examination showed separate, nonadherent grains from the cold runs in which a deflocculating agent was used; hence it follows that boiling [173]

[173] As it was Seger's practice to boil clays for the mechanical analysis, his results are affected by this error. Seger: Collected Writings, Am. Cer. Soc. Translation, pp. 45, 1108; 1902.

was too severe a treatment and reduced the size of grain by dissolving crystal matter.

The same effect is shown with the fire clay. With a cold sodium oxalate addition the results are quite different from those obtained after boiling with sodium oxalate. Under the microscope the crystal grains of the fire clay on 80-mesh and coarser sieves were apparently cemented aggregates, though each grain was a single mineral and not a conglomerate. The boiling dissolved crystal matter from the exposed surfaces, thus giving too small residues on elutriation.

With the more thoroughly disintegrated and plastic kaolins (Atlanta and Edgar) and ball and sagger clays, the colloid matter was present apparently in sufficient amounts to protect the crystal grains from solution in boiling tap water, and indeed the colloid matter was not fully removed by the tap water with any of the clays of this class. So the use of a deflocculating agent is imperative with the highly colloidal kaolins and ball and sagger clays.

It will be noticed where runs were made on the same clay with sodium hydroxide (NaOH) and sodium oxalate ($Na_2C_2O_4$); Harris, Knowles No. 12, and J. P. C. Co., Tennessee No. 9, that in each case less clay passed the third can when the sodium oxalate was used. This is attributed to the soluble salts in the tap water of the elutriator; they are precipitants for clay, and partly undid the work of the sodium oxalate.

A possible method of partial mechanical analysis is the use of immiscible liquids of appropriate specific gravity to separate the various constituents of clays by flotation. A number of experiments along this line were tried, using carbon tetrachloride or carbon disulphide (usually with some admixture of ether, to diminish the surface tension at the boundary with the aqueous phase); but, so far as these experiments went, the method was not very satisfactory.

D. DETERMINATION OF THE SOLUBLE SALTS IN CLAYS

Closely related to the question of the proper methods of mechanical analysis is that of the determination of soluble salts; the same influences affect both processes in comparable ways.

The main difficulty in soluble salts determinations has been to know when to stop. After such common salts as the sulphates of calcium, magnesium, and sodium, and sodium chloride have been removed by successive extractions with cold water, then without a break (or rather with decided overlapping) alkaline silicates are removed. While some of the alkaline silicates so removed are derived from the colloid portion of the clay, there is a tendency for the crystal portion of the clay to go over to the colloid form. This tendency is increased when hot water is used.

When extractions are made with a salt solution, metathesis, as we have seen, is likely to occur; even such insoluble substances as calcium phosphate are subject to decomposition by salt solutions. Hence extraction by salt solutions is inadmissible, as it is liable to give much more than the true water-soluble bases of a soil.

Schreiner and Failyer [174] remark that dried soils give up their soluble salts in somewhat greater concentration than fresh damp soils. Similar observations were collected by Ehrenberg.[175] Bleininger [176] in his investigations on destroying excessive plasticity by preheating clays, noted that heating the clays to 250 to 300° C seems greatly to facilitate movement of the soluble salts through the pores of the clay. These temperatures, which are necessary to drive off the hygroscopic water of the clays, decidedly increase the porosity of the clays. The gels "set" to a structure similar to that of charcoal.

Ries even found larger amounts of soluble salts in Wisconsin clays which had been soft burned than in the crude clays.[177] This may have been in part due to taking up sulphates from the fire gases or to oxidation of pyrites to sulphate.[178] Hard-burned clays yielded less than soft burned.

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[174] U. S. Dept. Agr., Bur. Soils, Bull. 31, p. 11.

[175] Z. Chem. Ind. Kolloide, 3, p. 201; 1908.

[176] Trans. Am. Cer. Soc., 12, pp. 513, 514; 1910.

[177] Clays of Wisconsin: Wisconsin Survey, Bull. 15, p. 22; 1906.

[178] Kerl-Cramer-Hecht, pp. 517, 518; 1907. According to Ost, Tech. Chemie, Berlin, p. 129; 1890; through Z. prakt. Geol., 11, p. 51; 1903. At Ampsin, near Liege, the acid fumes from roasting zinc ores are brought into contact with alum shales, whereby both potassium and aluminum are dissolved and alum is formed.

13, PROPOSED METHOD OF SOLUBLE SALT DETERMINATION

The following method of soluble salt determination is proposed as worthy of study:

Take 100 grams of air-dry clay, heat at 300° C for one hour, and weigh. (Or heat to constant weight at 105° C in air dried by bubbling through strong sulphuric acid.) The loss equals hydroscopic moisture. Crush to pass a 60-mesh sieve; put into a vessel containing one liter of cold water; shake one hour; let settle over night. Siphon or decant off a definite volume, even if turbid. Add from a burette a measured portion of magnesium sulphate just sufficient or a little in excess of the amount required to coagulate the clay sol. In aliquot portions of the resulting settled or centrifuged clear liquid the various determinations, including acidity, are to be made by usual quantitative methods. The silica present may necessitate an evaporation to dryness with hydrochloric or nitric acid. Organic compounds may require special treatment or ignition. From the total sulphuric anhydride found is to be subtracted that added as magnesium sulphate. If we assume that no magnesium was present as a soluble salt, which is nearly the case in the presence of a turbid solution, we may assume that the magnesium added as sulphate minus the magnesium found equals the magnesium used in coagulating the clay; also that from the alkali found is to be deducted an amount equivalent to the magnesium used in coagulating the clay.

E. SCUM ON CLAY WARES AND ITS PREVENTION

Soluble salts are the cause of scum when they are carried to the surface of the clay and are deposited there on evaporation of the water. Now, colloidal matter opposes to some extent the flow of solutions through it; especially it slows down the rate of diffusion of salt solutions through it. Indeed, the studies of Bechhold [179] (and of others since his time) on the process now termed "ultrafiltration" indicate that the pores of a colloidal medium may be of such dimensions as not only to retard but actually to retain the larger molecules.

Hence, even though analysis should indicate a fairly high content of soluble salts, a brick made from such clay may not scum if

[179] Zs. physik. Chem., 66, pp. 257–318; 1907.

the clay has sufficient colloidal material in a suitable condition to prevent the appearance of the soluble matter at the surface. Their appearance at the surface is in part conditioned by the manner of drying. For instance, A. F. Greaves-Walker [180] writes:

> Where a clay contains soluble salts, they are not deposited on the surface at all, or at least to a less degree, where the drying is steady and rapid than where it is slow and discontinuous.[181] It seems that rapid drying causes the water to come through the pore channels of the clay as through a filter and a sort of osmosis is set up, by which the saline matters are retained inside the mass of the clay while the water escapes as vapor from the outside. But where the drying is slow the salts get through this barrier and arrive on the surface plentifully.

On the other hand, drying must not be too rapid, for, according to Orton [182]—

> Rapid drying of clay wares must not proceed much faster than capillary flow. Practically we always have a strain on the drying surface. If the tensile strength is good, the surface will stand under the strain until the float water is removed. * * * Glass pots are blanketed, and uncovered for an hour at a time for evaporation. While blanketed, capillary flow is bringing more moisture to the surface.

14. USE OF BARIUM CARBONATE TO PREVENT SCUM

Of the salts commonly found in clays, only the sulphates require consideration as the cause of efflorescence on fired ware.[183] The difficulty caused by soluble sulphates can be obviated by adding barium carbonate. But another difficulty arises—how to determine the proper quantity to add, for barium carbonate, besides reacting with the soluble sulphates, will also react with some of the colloidal matter present, in each case with the simultaneous formation of a (probably soluble) carbonate of the base displaced. There is every reason to believe that the barium carbonate acts first upon the soluble sulphates, and secondly upon the colloids. Indeed, Dutoit and Duboux [184] have shown this to be so in the case of wines. If the amount of sulphuric anhydride in the clay has been accurately determined, it would seem that the theoretically equivalent amount of barium carbonate might be added. If the clay were worked sufficiently after the addition of barium carbonate, it is conceivable that the reaction between the slightly soluble barium carbonate and the sulphates would be nearly com-

[180] J. Ind. Eng. Chem., 2, p. 375; 1910.
[181] Kerl-Cramer-Hecht, p. 517; 1907.
[182] Private Notes on Lectures at Ohio State University.
[183] Kerl-Cramer-Hecht, p. 517; 1907.
[184] Schweiz. Wochschr., 46, pp. 672–678; Chem. Abstracts, 3, p. 469; 1909.

plete. That this is unlikely to be so in practice is probably the reason for the direction given by Seger [185] to use twice the theoretical quantity. The necessity of a double quantity may also be due to a reaction with the colloidal material, or to both causes together.

Another reason hitherto unrecognized is the simultaneous formation of alkaline carbonates mentioned above; these tend to deflocculate the clay and thus to lessen the plasticity. But if an excess of barium carbonate is used, it will inhibit this deflocculation and thus preserve the plasticity.

"*Practical*" *Test.*—The "practical" test for the barium carbonate requirement of a clay, consisting in adding to equal weights of clay a series of increasing weights of barium carbonate, shaking with water, and finding which members of the series completely precipitate all the barium added, is liable to lead to wasteful use of barium carbonate by reason of the combination of the latter with the harmless colloids of the clay.

Hirsch [186] made an excellent study of this test. While he did not understand the cause of the excessive taking up of barium, he found a means of combating it. He directed that 4 grams aluminum chloride be used in the test with 100 grams clay and that the test with barium would then be "faultless." The action of the aluminum chloride is to combine with the colloids and render them so insoluble that they are not affected by the barium carbonate, which consequently under these conditions reacts only with the soluble sulphates.

F. CASTING PROCESS

In the casting process for the manufacture of clay wares the clay body, made into a slip of creamy consistency with water, is poured into a plaster-of-Paris mold. The mold absorbs the water rapidly from the slip in contact with it, and a layer of the clay body forms on the surface of the mold. When the layer reaches the desired thickness the excess of still liquid slip is poured out. On standing longer the formed ware loses some more water to the plaster and shrinks sufficiently to come loose from the mold.

[185] Keil-Cramer Hecht, p. [illegible], 1907.

[186] Tonindustrie-Zeitung, 28, p. 491, 1904. U. S. Geol. Survey Bull., 388, pp. 37–39, 1909.

Obviously the less the amount of water in the slip the quicker the layer will form on the plaster, the less drying of the molds will be required, and the molds may be filled at more frequent intervals. This process is used on the one hand for table and sanitary ware and on the other hand for the manufacture of high-grade refractories, such as glass pots.

15. USE OF ALKALI TO DECREASE WATER REQUIREMENT

A bulky highly colloidal clay exhibits a large shrinkage when the water is given up again by drying and evaporation. When such a bulky clay is treated with soluble hydroxides or other alkaline precipitants so as to form the alkali compounds of the colloid matters, it usually requires only about half as much water to bring it to the creamy consistency of a casting slip as would be required for the clay in its ordinary condition. The clay also loses its plasticity.[187] In other words, when the alkali compounds of the clay colloids are dissolved or suspended in water, plasticity is absent; in the sol (deflocculated) condition they are quite fluid. Kosmann[188] first suspected the solvent effect of the alkaline addition. He thought that a "certain part of the silica in the clay substance is dissolved by the soda and by the removal so effected of these intervening silicic acid particles a mechanical alteration of the mass is effected in the sense of dilution and greater mobility." If we include with silicic acid the other colloidal constituents present, the portion of Kosmann's views above given is correct.

Zebisch[189] attributed the diminished water requirement of casting slip when alkali is used to a depression of the capillary coefficient, and asserted that, on the other hand, acid solutions, with a greater coefficient, will penetrate between the clay particles to a greater extent. The Landolt-Börnstein tables (second edition) fail to show any acid or alkaline solution with a capillary coefficient greater than that of water. Zebisch's explanation of the greater density of casting slips when alkali is used is therefore unconvincing.

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[187] Kerl-Cramer-Hecht, pp. 279, 305; 1907. Seger: Collected Works, Am. Cer. Soc., translation, p. 722; 1902.

[188] Tonind.-Ztg., p. 382; 1895. Kerl-Cramer-Hecht, p. 307; 1907.

[189] Sprechsaal, p. 1005; 1894; pp. 303 et seq.; 1895. Kerl-Cramer-Hecht, p. 306; 1907.

Hitherto the choice of deflocculants for the casting process has been almost wholly an empirical process. Weber,[190] whose patented casting process for glass pots and other refractories is used in more than 20 factories, after describing the use of alkalies, the sodium salts of carbonic, phosphoric, oxalic, and boric acids, barium hydroxide, and calcium hydroxide, said:

> Which of the above-named alkalies should be used, and the quantity, must be found out for each clay separately according to its position.

Foerster[191] noticed that calcium sulphate hinders the action of alkalies in preparing clays for casting and that its effect can be offset by the use of a precipitant for lime, as sodium carbonate. Weber[192] patented the use of precipitants for calcium sulphate. In his specification he gave the following example, which shows that he is not clear as to the difference in action of alkali hydroxides and of alkaline precipitants:

> 450 kg fat refractory Stourbridge clay and chamotte.
> 0.350 kg barium hydroxide, $Ba(OH)_2+8H_2O$, or
> 0.220 kg barium carbonate, $BaCO_3$.
> 120 kg water.
> 0.600 kg sodium hydroxide ($NaOH$), or the corresponding amounts of sodium carbonate (Na_2CO_3) or sodium silicate ($Na_2O.xSiO_2$).

16. CHOICE OF DEFLOCCULANT

The methods given in this paper make it possible to determine, first, what amounts of soluble salts are in the clay; second, what bases are combined with the gel; and, third, what reagents are best suited chemically to react with these, and to dissolve the colloid matter of the clay.

17. JOINT USE OF SODIUM CARBONATE AND SODIUM SILICATE

Fig. 22[192a] illustrates the separate and joint action of sodium carbonate and sodium silicate on a ball clay and a china clay and a body made from them. The proportions used in ordinary work while variable, and determined by tradition or experiment, are about 0.1 per cent of each. The lower right-hand figure shows that the deflocculation is not complete at this concentration. While Böttcher says that he successfully cast a stoneware clay

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[190] Trans. Eng. Cer. Soc., 8, I, p. 16, 1909.
[191] Luc chem. Ind., 28, pp. 733–740, 1965.
[192] Brit. pat. 6560 (Mar. 18, 1909).
[192a] See p. 56.

with the proportion of sodium hydroxide giving maximum deflocculation, it should be determined practically whether this point or some point short of it gives best results.

In studying Fig. 22, one naturally tries to find what ratio of sodium carbonate to sodium silicate is most advantageous, or whether one should be used exclusively. The reasons are not evident from the diagram. If sodium carbonate is used alone, the stream when poured into the mold breaks into numerous drops. This causes the entanglement of air bubbles. Wherever one of these air bubbles gets into the ware, a crack will develop, and a piece of ware be ruined. If sodium silicate is used alone, the slip is liable to flow in strings like thick sirup. A proper balance between these two effects is secured by using a suitable mixture of the two reagents. The slip will then pour in a clean-cut solid stream, with but slight tendency to draw in air bubbles.

The writer is informed that some three plants making sanitary ware of fire clay have tried and abandoned Weber's process. Their difficulties were said to be (1) that ware made by the process was "rotten" or lacking in strength; (2) that the fine material of the clay seemed to collect at the surface, leaving only large grains in the center; (3) that the ware stuck to the molds; and (4) that the plaster of the molds was rapidly attacked.

The first and third objections indicate that the plasticity was too thoroughly destroyed; that it would have been better, therefore, to use less reagent, and so to retain some of the plastic strength of the clay. The fourth objection also indicates the use of reagent in excess of the amount that the clay would react with.

The second and third objections the writer has found to occur with a No. 1 fire clay treated with just sufficient reagent to give maximum deflocculation. In the writer's experiment with this fire clay the water requirement was the same with or without the alkaline addition.

It would appear that for the casting process a certain amount of shrinkage is essential in order that the ware may free itself properly from the molds; so that the clay must originally have sufficient of the constituent that shrinks (colloid), and consequently that the shrinkage must not be unduly suppressed by the alkaline addition.

18. ADDITION OF SOAP TO POTTERY BODIES

Soft soap is occasionally added to pottery bodies to make them more suitable for casting.[193] Trouble is occasionally experienced in a pottery when through mischance or malice soap gets into a blunger of clay and causes a decrease in plasticity.

While the best condition for casting appears to be somewhat short of total deflocculation, the converse is not necessarily true for plastic working. It is true that the gel must be present in suitable amount for good working properties; but whether the presence of some sol is advantageous is not known.

In Sprechsaal, page 1049, 1903, several correspondents tried to assist a questioner who found his casting body thicker after adding soda. One thought he used too much soda. A second said that a clay containing organic acids is not suited for casting. A third suggested that perhaps it had been acidified for turning and so neutralized the soda; or that the water contained some salt precipitated by carbonate of soda. The fourth said that clays carrying hydrated silicic acid are unsuited for pouring. "The more soda one uses the more gelatinous the mass becomes."

G. REGULATION OF GLAZES AND ENGOBES

Glazes are mixtures composed largely of alkaline silicates, natural or artificial. If the amount of alkali present is sufficient to keep the colloidal material in suspension, there is danger that the crystal and glassy grains may fall to the bottom of the dipping tub and set so firmly as to cause the dipper much trouble. The condition desirable in a glaze is that all the colloidal material should be in the form of a thin jelly, which then holds up the granular matter. This condition may be obtained either by the addition of coagulants or thickness, for which purpose the following have been used.[194]

Coagulants: Barium(?), strontium and magnesium sulphates nitric,[195], sulphuric, hydrochloric and boric acids; and vinegar.

Thickeners: Blood, milk, sirup, dextrin, gum arabic, plastic clay.[196]

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[193] Karl Cramer-Hecht, p. [illegible], 1[illegible].

[194] A. E. Mayer, Trans. Am. Cer. Soc., 11, pp. 169-174, 1909.

[195] Nitric acid forms a poisonous compound with lead, if present.

[196] Langenbeck, Chemistry of Pottery, p. 124; 1895.

Calcium nitrate, ammonium nitrate, and ammonium carbonate are also said to be effective coagulants, especially the last;[197] and starch and common flour paste are used as thickeners. According to Jul. Grünwald,[198] the best coagulants are ammonium carbonate, magnesium oxide, and borax.

Even when a glaze has almost set, the grinding may be continued after a small addition of hydrochloric acid, nitric acid, barium chloride, or calcium chloride.[199] In France, sea salt is added to porcelain glazes,[200] also vinegar [201] to the glaze for frit porcelain.

The following materials are used in the manufacture of glazed oven tile:[202] Common salt, sodium nitrate, potassium nitrate, which act as coagulants; borax, sodium carbonate, potassium carbonate, which act either as deflocculants or coagulants, according to the amount used. Addition of common salt has in this case the further effect of improving the color by reacting with the iron to form a volatile chloride.

Carter [203] called white lead "a raw flotative ingredient." In the writer's experience the "Old Dutch process" white lead, by reason of its bulky colloid nature, stays in suspension much better than some of the denser crystalline rapid process white leads. Similarly the natural bulky English cliffstone paris white stays in suspension better than some of the more crystalline precipitated calcium carbonates.

Both the thickeners and the coagulated gels also act as adhesives; the additions are sometimes made principally for this latter purpose.[204] With engobes in particular, but often with glazes, a third function of the addition is often to regulate the shrinkage of the slip or glaze. For instance, Seger [205] introduced colloidal alumina into a glaze in order that its shrinkage might produce the craquelé effect.

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[197] Kerl-Cramer-Hecht, pp. 342, 350, 353; 1907.
[198] Keramische Rundschau, pp. 358–359; 1910.
[199] Kerl-Cramer-Hecht, p. 1149; 1907.
[200] Ibid, p. 1405; Keramic Studio, p. 172; 1903.
[201] Kerl-Cramer-Hecht, p. 1509; 1907. Keramic Studio, p. 172; 1903.
[202] Kerl-Cramer-Hecht, p. 1085; 1907.
[203] Trans. Am. Cer. Soc., 5, p. 293; 1903.
[204] Kerl-Cramer-Hecht, pp. 1004, 1006, 1007; 1907.
[205] Collected Writings. Am. Cer. Soc., Trans., p 733; 1902.

The shrinkage will be a minimum when that proportion of deflocculant is used which produces maximum sol formation; it will increase with either smaller or larger amounts of reagent, and, in the latter case, may or may not reach, or exceed, that of the untreated material.

The effect of substances which act only as coagulants, upon a mixture containing some sol, is to increase the shrinkage. Substances that act only as thickeners and adhesives will tend to increase the shrinkage.

Ammonia is the only substance which in general acts only as a deflocculant; though in sufficiently great concentrations, even it produces coagulation. The other alkalies and alkaline precipitants act as deflocculants or coagulants according to the amount used. The simple mineral acids and most salts act as coagulants only. Silicate of soda is a deflocculant, thickener, and adhesive. Gum arabic and gum tragacanth appear to be thickeners and adhesives only; sour milk appears to be both a thickener and coagulant.

19. SHRINKAGE REGULATION

According to Geijsbeek[206]—

> An engobe on biscuit body should be so compounded that its shrinkage should be nothing, because the body on which it is applied does not shrink any more. An engobe for stoneware has to shrink at the same rate as the shrinkage of the stoneware body on which it is applied.[207] In making an engobe on green ware, we have to use some plastic clay.

Many have observed that the result of the use of highly colloidal materials (obtained either naturally or by very fine grinding) is to increase the bulk[208] and shrinkage[209] of glazes, thus producing cracking,[210] crawling,[211] peeling,[212] and rolling up,[213] or beading[214]

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[206] Trans. Am. Cer. Soc., 6, p. 210; 1904.

[207] Seger, Collected Writings, Am. Cer. Soc. Trans., pp. 438, 622, 626, 628; 1968. Stull, Trans. Am. Cer. Soc., 12, p. 713; 1910. Bourry: Treatise on Ceramic Industries, p. 236; 1901.

[208] Ashley, Trans. Am. Cer. Soc., 9, p. 56; 1907.

[209] Hottinger, Trans. Am. Cer. Soc., 2, p. 132; 1900. Ashley, ibid., 12, p. 444; 1910.

[210] Seger, Collected Writings, Am. Cer. Soc. Trans., p. 589; 1902. Carter, Trans. Am. Cer. Soc., 5, p. 293; 1903. Geijsbeek, ibid., 4, p. 51; 1902.

[211] Purdy, ibid., 4, pp. 66, 70, 74; 1902.

[212] Carter, ibid., 5, p. 293; 1903.

[213] Seger, Collected Writings, p. 1147. Ashley, Trans. Am. Cer. Soc., 9, p. 56; 1907.

[214] Carter, ibid., 5, p. 293; 1903.

when too thickly applied[215] or when sweated in drying or in the early stages of burning.[216] The ill effects of sweating are probably due to the condensation of acids from the combustion gases upon the glaze or engobe.[217]

These defects may be overcome by selecting less plastic clays,[218] by calcining some of the clays, by using less clay ,[219] by adding granular materials,[220] by coarser grinding, by dry grinding,[221] by diluting the glaze, soaking the bisque ware, or dipping the green ware at an earlier stage of drying [222] (any of which makes the layer taken up thinner),[223] or by using a deflocculant.[224]

Deflocculants may be used in glazes or engobes to be applied to bisque bodies, as they decrease the amount of colloidal material and so cut down shrinkage. Their use is not common for this purpose. The quantities giving the best effects are so minute that an experimenter would ordinarily use too much, and so entirely miss the effect.

As some substances are either deflocculants or coagulants, according to the amounts used and the nature of the mixture to which they are applied,[225] it is not always easy to decide which is the case with an example taken from ceramic literature; but generally enough reagent is used to cause coagulation.

20. LACK OF ADHESION

On the other hand, some very similar faults occur when there is a deficiency of colloids in the glaze or engobe or when the colloids present are in the sol form. A lack of adhesion [226] to the ware may be due to a lack of gel in the glaze, to dust or oil on the

[215] Seger, Collected Writings, p. 589. Purdy, Trans. Am. Cer. Soc., **4**, p. 74; 1902. Carter, ibid., **5**, p. 293; 1903. Binns, ibid., **11**, p. 170; 1909.

[216] Purdy, ibid., **4**, p. 74; 1902. Stull, ibid., **12**, p. 72[38] 1910.

[217] Seger, Collected Writings, p. 217.

[218] Geijsbeek, Trans. Am. Cer. Soc., **4**, p. 52; 1902. Jackson, ibid., **11**, p. 171; 1909.

[219] Purdy, ibid., **4**, pp. 66, 74; 1902; **11**, p. 169; 1909. Binns, ibid., **11**, p. 170; 1909.

[220] Geijsbeek, ibid., **4**, p. 51; 1902. Purdy, ibid., **11**, p. 169; 1909. Kerl-Cramer-Hecht, p. 1187; 1907. Seger, Collected Writings, p. 1147. Binns, Trans. Am. Cer. Soc., **11**, p. 170; 1909.

[221] Carter, ibid., **5**, p. 293; 1903.

[222] Stull, ibid., **12**, p. 714; 1910.

[223] Seger, Collected Writings, p. 439. Shaw, Trans. Am. Cer. Soc., **11**, p. 121; 1909. Purdy and Brown, ibid., **11**, p. 237; 1909.

[224] Stull, ibid., **12**, pp. 718, 763; 1910.

[225] Stull, Trans. Am. Cer. Soc., **12**, p. 723; 1910.

[226] Seger, Collected Writings, pp. 623, 627.

ware,[227] to crystals of soluble salts at the surface of the ware,[228] to a lack of porosity of the body,[229] or to a lack of fluxes to cause the fired engobe to adhere.[230] Such faults are known as crawling,[231] scaling,[232] flaking,[233] beading,[234] and especially as dusting[235] or rubbing.[236]

They are obviated by adding adhesives such as gum tragacanth,[236] ball clay in place of china clay,[237] plaster of Paris before setting,[238] mucilage,[239] dextrine (3 per cent)[240] glue,[241] sirup or sugar water,[242] glycerin,[243] ox blood,[244] potato starch (2 per cent),[245] by coagulating the sol (which is in a way equivalent to adding adhesives) by such coagulants as borax in excess,[246] sodium carbonate in excess,[247] plaster of Paris,[248] salsoda (2 per cent),[249] magnesium sulphate,[250] or boric acid.[251]

In some cases it is thought by the users that these added salts themselves act as adhesives;[252] that when they crystallize the crystals hold the whole together.[253] This is possible, but in most cases unlikely.

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[227] Ibid., pp. 588, 627, 1115. Purdy, Trans. Am. Cer. Soc., **4**, p. 74; 1902. Stull, ibid., **12**, p. 713; 1910.

[228] Seger, Collected Writings, p. 1147; 1902. Hottinger, Trans. Am. Cer. Soc., **9**, p. 520; 1907.

[229] Seger, Collected Writings, p. 588.

[230] Ibid., p. 450.

[231] Purdy, Trans. Am. Cer. Soc., **5**, pp. 161, 162; 1903. Barringer, ibid., **5**, p. 265; 1903. Stull, ibid., **10**, p. 241; 1908.

[232] Seger, Collected Writings, p. 589. Hottinger, Trans. Am. Cer. Soc., **9**, p. 520; 1907.

[233] Stover, Trans. Am. Cer. Soc., **11**, p. 172; 1909. Stull, ibid., **10**, p. 220; 1908; **11**, p. 607; 1909.

[234] Purdy, ibid., **5**, p. 162; 1902. Stephani, ibid., **11**, p. 615; 1909. Stull, ibid., **11**, pp. 611, 615; 1909.

[235] Purdy, ibid., **4**, p. 75; 1902.

[236] Purdy and Krehbiel, Trans. Am. Cer. Soc., **9**, p. 337; 1907. Worcester, ibid., **10**, pp. 452, 482; 1908. Orton, ibid., **10**, p. 561; 1908 (3 g per l.). Taxile Doat, Keramic Studio, p. 78; 1904.

[237] Purdy, Trans. Am. Cer. Soc., **4**, p. 75; 1902. Stull, ibid., **11**, p. 607; 1909. Seger, Collected Writings, p. 624.

[238] Purdy, Trans. Am. Cer. Soc., **4**, p. 75; 1902.

[239] Seger, Collected Writings, pp. 471, 472. Binns, Trans. Am. Cer. Soc., **5**, p. 52; 1903.

[240] Stull, ibid., **10**, p. 220; 1908.

[241] Stephani, ibid., **11**, p. 615; 1909.

[242] Seger, Collected Writings, p. 628.

[243] Ibid., pp. 631, 634.

[244] Ibid., p. 1115.

[245] Kerl-Cramer-Hecht, p. 1102; 1907.

[246] Purdy, Trans. Am. Cer. Soc., **4**, p. 75; 1902; **5**, p. 162; 1903. Stull, ibid., **10**, p. 241; 1908; **11**, pp. 611 615; 1909. Kerl-Cramer-Hecht, p. 1102; 1907.

[247] Purdy, Trans. Am. Cer. Soc., **4**, p. 75; 1902. Stull, ibid., **11**, p. 615; 1909.

[248] Purdy, ibid., **4**, p. 75; 1902. Stull, ibid., **11**, p. 615; 1909. Stephani, ibid., **11**, p. 615; 1909.

[249] Purdy, ibid., **5**, p. 161; 1903.

[250] Shaw, ibid., **11**, p. 521; 1909.

[251] Stephani, ibid., **11**, p. 615; 1909.

[252] Barringer, Trans. Am. Cer. Soc., **5**, p. 265; 1903; 5 per cent sodium carbonate, borax, calcium sulphate, cobalt chloride. Orton, ibid., **10**, p. 561; 1908; sodium carbonate, borax, plaster of Paris.

[253] Purdy, ibid., **4**, p. 75; 1902.

Bleininger [254] suggested that, in some of these cases, the added salt may undergo a Sorel cement reaction with part of the glaze.

That the action of adhesives upon clays is essentially different from that of deflocculants and coagulants was demonstrated by treating a ball clay, a china clay, a feldspar, and a quartz with gum tragacanth. In one series the gum used was dissolved in cold water; in the other series hot water was used. The solution in cold water was very imperfect; the gum would settle with the clay, etc., and by its own bulk increased the bulk of the sediment. The solution in hot water seemed homogeneous, and the gum was not a constituent of the sediment. It did not prevent the sedimentation of the clay, though the process was less rapid because of the increased viscosity of the medium. But in none of these series with gum tragacanth was any deflocculant or coagulant effect noticed. Fickendey [255] found starch to be without influence.

Feldspar, because of its alkalinity, tends to assume the sol state. It has been found to cause cracking,[256] crawling,[256-257] and beading.[257] The remedies proposed are decrease of feldspar,[257] replacement by Cornwall stone [258] (which, having been subjected naturally to leaching, has less readily soluble matter), and addition of whiting [257] (the varities of which used in potting usually have a notable gel content).

In some cases, owing to the refractoriness of a Bristol glaze or engobe, it fails to adhere in firing. The remedy in such cases is to add fluxes [258] or to decrease the proportion of constituents which are present in too great amount to exert their best fluxing action.[259] Some of the additions made for other purposes are also fluxes, such as borax, soda ash, etc. The refractoriness of an excess of zinc oxide may explain the following observations:

Purdy [260] says: "To zinc many ascribe all the responsibility for the manifestations of crawling." Later he says that it may be due to too high zinc oxide. Stephani [261] says beading in the kiln

[254] Private notes on lectures by Edward Orton, jr., at Ohio State University; 1905.
[255] J. Landw., **54**, p. 345; 1906.
[256] Fackt. Trans. Am. Cer. Soc., **11**, p. 615; 1909.
[257] Purdy, ibid., **5**, p. 162; 1903.
[258] Seger, Collected Writings, p. 589. Private notes on a lecture by R. T. Stull; 1905. Bourry, Treatise on Ceramic Industries, p. 236; 1901.
[259] Stull, Trans. Am. Cer. Soc., **12**, p. 764; 1910.
[260] Purdy, ibid., **4**, p. 70; 1902.
[261] Ibid., **11**, p. 615; 1909.

may be prevented by replacement of zinc oxide by magnesia. Eleod [262] overcame flaking by calcining a portion of glaze containing all the zinc oxide.

Purdy [263] stated that "BaO (used as barium carbonate) is more potent than CaO (used as whiting) in producing flakes."

Seger [264] added glaze to an engobe to increase its adhesion to the fired body.

Stull [265] has explained in detail the remedies for the various defects of engobes. From his cases 16 and 24 it appears that some engobes sinter onto the ware, and then if subjected to still higher temperatures the additional fire shrinkage causes them to craze or flake off if not very firmly attached by the fluxes.

H. MISCELLANEOUS APPLICATIONS

A few miscellaneous applications of the principles discussed in this paper are included; some are no more than suggestions, but they are given for what they are worth.

21. WATER PURIFICATION

Clays may be present as an impurity of water supplies, or they may be used as a means of removing other impurities, such as mineral bases that produce incrustations in boilers.

This twofold rôle is readily explicable on the views advanced in this paper. Roughly speaking, when the clay content of a river is high the soluble salt content is low, and when the soluble salt content is high the clay content is low. As the lowest amount of soluble salts and highest proportion of suspended matter come at the high-water stage of a river, the suspension might be and usually is attributed to the extra carrying power of water with the increased velocity that accompanies a high stage. But with a high stage the water of a river is greatly diluted. A sufficient degree of dilution, it has been shown (p. 55), will enable even still water to hold in solution or suspension very decided amounts of soluble clay colloids. The solvent action at least supplements the mechanical tendency to suspension.

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[262] Ibid., 11, p. 174; 1909.

[263] Trans. Am. Cer. Soc., 11, p. 169; 1909.

[264] Collected Writings, pp. 624, 627, 629.

[265] Trans. Am. Cer. Soc., 12, pp. 703, 704; 1910. See also Bourry, Treatise on Ceramic Industries, pp. 295–298, 315–316; 1901.

Atterberg [266] said:

Spring waters in general contain some salt and therefore are usually clear, even when they come from clayey soils. The waters of mines and streams are, on the other hand, weaker in salts and always turbid with clay particles.

Schloesing [267] said:

It is then to the presence or to the absence of these salts that it appears natural to attribute the limpidity or the troubled character of the filtered liquid.

Further: [268]

There are rivers that are habitually turbid with soil, among others the Garonne and the Loire; analysis shows that their waters are too poor in salts of the alkaline earths. According to M. H. Sainte-Claire Deville, the content of lime and magnesia of our principal rivers are, on the average, the following:

	Seine	Rhone	Garonne	Loire
	mg	mg	mg	mg
Lime (per liter)	104.0	63.4	36.1	27.0
Magnesia (per liter)	1.3	4.5	1.6	2.9

These figures, approaching those given above as necessary to produce coagulation, show that the water of the Seine ought to deposit its soil in a few hours; those of the Rhone in a sensibly longer time; those of the Garonne and of the Loire do not clear.

Public water supplies should contain 70 to 80 mg of lime per liter in order to clarify spontaneously in sedimentation basins.

(*a*) USE OF COAGULANTS TO REMOVE CLAYS

The natural settling of a turbid water is usually too slow a process for economical work at purification plants. To many waters which exhibit permanent turbidity are added salts of those bases which form insoluble precipitates with clay sols; for instance, addition of lime or alum effects a rapid sedimentation.

The reagent chosen should form a coagulum of minimum solubility and a soluble reaction product with a minimum of undesirable properties. For example, the effect of alum in coagulating the sodium sol may be written

$$\underset{\text{(soluble)}}{Al_2SO_4} + \underset{\text{(soluble)}}{\text{Na sol}} \rightarrow \underset{\text{(insoluble)}}{\text{Al gel}} + \underset{\text{(soluble)}}{Na_2SO_4}$$

[266] Landw. Vers. Sta., 69, pp. 93–143; 1908.

[267] Encyclopedie Chimique, M. Fremy. Tome X. Applications de Chimie Organique. Contribution a l'Etude de la Chimie Agricole, par M. Th. Schloesing. Paris, V^ve^ Ch. Dunod, Editeur, Quai des Augustins, 49; 1888. Du sol, p. 62.

[268] Ibid., p. 65.

Some reagents, while forming the desired insoluble coagulum, give poisonous soluble reaction products or are themselves poisonous, and hence may not be used (e. g., lead nitrate).

In practice it is necessary to leave some soluble salt in the water in place of the clay sol removed. In substantially all turbid waters there are present bases which, under proper conditions, can coagulate clay sols;[269] but to effect satisfactory clarification, it is necessary always to add a sufficient excess of reagent.

(*b*) USE OF CLAY TO REMOVE BASES

Clay has also been used for many years to remove bases such as iron from water supplies. The reaction involved is again a simple exchange of bases, altogether analogous to the reaction with alum mentioned above. If we assume that a partial removal of the soluble iron salts is sufficient, the water will probably be clear at the end of the process; but if an excess of soluble clay is used the water will be left turbid. Incidentally it may be noted that turbidity of quiet water is an indication that the water contains a very small proportion of soluble salts.

If good mechanical stirring arrangements are available, an acid clay might be added to a water containing iron salts without producing permanent turbidity; this may be illustrated by the following scheme:

$$\underset{\text{(soluble)}}{FeSO_4} + \underset{\text{(insoluble)}}{H\ \text{gel}} \rightarrow \underset{\text{(insoluble)}}{FeGel} + \underset{\text{(soluble)}}{H_2SO_4}$$

J. G. Roest [270] found 1.5 per cent potter's clay sufficient to precipitate suspended matter from the waste waters of pulp mills. The precipitate has an appreciable value as a fertilizer.

It is a common practice to use kaolin as a precipitant where, in most cases, the less expensive, more plastic clays would be more effective, since the colloid content is the active agent.

22. ADDITION OF ACID DISINFECTANTS TO MODELING CLAYS

In preparing modeling clays, it is sometimes desirable to add a disinfectant (for use in public schools, etc.). In such cases a compound of acid nature is to be preferred, in order that the plasticity shall not be lessened by the addition.

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[269] For example, see R. B. Dole: The Quality of Surface Water in the United States. I. Analyses of Water East of the 100th Meridian. U. S. Geological Survey, Water-Supply Paper 236, 1909.

[270] Chem. Weekblad, 6, pp. 106–109; Chem. Zentr., 1909, I, 796; C. A., 4, p. 3110; 1910.

23. USE OF SOAP FOR CLEANSING

On a previous page (p. 75) are given the results of a series of experiments on the effect of soap on clays. From these the practical conclusion, as applied to laundry work, is that a given soap will do the best work with dirt of the nature of clay on cloth when a particular concentration of soap in water is used. A less concentration will be ineffective in loosening dirt. A greater concentration, as when soap is rubbed on a badly soiled spot, though reaction takes place, is not at first effective because of salting out; but when the cloth is rinsed out in pure water the concentration is thereby diminished, and so passes momentarily through the strength giving the strongest solvent effect. Practical experience has shown that a mixture of solvents is often more effective than soap alone, for example; gasoline in the soapy water assists with greasy dirt; borax, soda, etc., are of value in particular cases.

24. CLEANING BRICK FRONTS

The cleaning of the fronts of brick buildings is often a vexatious problem in smoky cities. According to the British Clayworker,[271] the "present foolish custom of sandblasting brick fronts" leaves all brick, excepting the very hardest sorts, in such condition that they are soon dirtier than before. "A soap wash, followed by an acid solution," would serve the purpose better, and at one-fifth of the amount expended. These conclusions were verified by means of a series of comparative tests made on the walls of the old Arsenal buildings at the Pittsburg Testing Plant. Cold solutions (0.5, 1, 2, 5, and 10 per cent) of a common laundry soap (Colgate's Octagon) were used, and the conditions of application were made as uniform as possible. From these tests it appears that the 1 per cent solution gives the best results, as in this case nearly all of the soot was removed, and the bricks had nearly regained their original red color. The effect of adding kerosene to the 1 per cent soap solution was also tried; but it was found that even with 1 per cent kerosene added the results were not so good as with the soap solution alone.

[271] British Clayworker, 19, Brickbuilder, 25, 1910.

25. POLISHING PLATE GLASS

Plate glass is polished with water and rouge, an iron oxide prepared by calcining sulphate of iron. It is found in practice that the rouge does not work well unless it has a certain acidity, and that much of it is carried off by the waste waters from the polishing process. Now the water used with the rouge dissolves the alkali from the freshly exposed face of the glass; so that it is easily conceivable that the alkali first neutralizes the acidity of the rouge, then reaches such a concentration as to cause the suspension and loss of the rouge. This suggests that by a continuous supply of acid during glass polishing, the alkali could be kept neutralized; the rouge would then be kept in a coagulated condition, and so would not be wasted so readily by outflowing water. It may, on the other hand, be true that the rouge now flowing away would not be of value for longer periods of use and that a more rapid attack by acid would give an inferior polish. However, the practicability of the suggestion could easily be tested.

26. FULLER'S EARTH

Fuller's earth may be defined as clay of especially high absorptive powers or colloid content. There are many varieties, and the possibilities of improving or regulating it are many. As its action is in many cases an exchange of bases, the first idea is to see to it that one's earth has the base best adapted to the specific purpose in view, either by selecting it or by treating with salts.

If it is not sufficiently porous for most effective working, it may be made so by heat treatment. This sets the colloids without destroying their reactivity in most cases. The structure of the gels of certain fuller's earths, however, is so much altered even by drying out at ordinary temperature as to make them worthless. This accounts for the differences of opinion noted in technical literature concerning the desirability or uselessness of heating fuller's earth. The silicate and the humus colloids are probably unharmed by heat, while the iron hydroxide, alumina, and silica colloids probably lose in activity. The point is worth investigation.

A concentrated fuller's earth may be prepared from any clay by dissolving out the colloid matter and recoagulating it. It is

possible that some clay washing plants may obtain an artificial fuller's earth as a by-product by coagulating the clay waters that ordinarily refuse to settle on standing, and now run to waste.

27. KAOLIN AND FULLER'S EARTH AS ANALYTICAL REAGENTS

Various clays have been employed as absorbents in agricultural analysis, e. g., kaolin in the determination of tannin in tanning extracts and liquors [272] and in tea,[273] and in the determination of alcohol in flavoring extracts;[274] fuller's earth, for the determination of caramel in vinegar,[275] vanilla,[276] etc.

In each case unexplained difficulties occur in practice, and the methods are looked upon with more or less suspicion. This is but natural, as the action of the clay in each case resides in a colloid constituent present in unknown amount (high with the fuller's earths, low with kaolins) and combined with more or less easily replaceable bases.

It would therefore seem advisable that for such determinations the same amount of colloid matter (as determined by the malachite green oxalate test, for example) should be taken each time, rather than equal weights of clay; further, that by treatment with appropriate salt solutions, those bases giving more favorable action should be put into the colloid matter.

According to Jennison: [277]

> When a solution of a dyestuff, more particularly the basic colors, is added to starch, clay, green earth, etc., a certain amount of coloring matter is taken up.

He does not consider the action as due to any chemical attraction, and condemns the colors produced as fugitive, lacking fullness and brightness. Hundeshagen, however, has found some dyes to be very strongly held by minerals. Further on Jennison [278] states that lakes formed with less than the theoretical amount of tannic acid are fugitive; yet a stable, satisfactory, though duller color, is obtained by using the theoretical amount. We have

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[272] U. S. Dept. Agr., Bur. Chem., Bull., **99**, pp. 123, 124, 1906.
[273] Ibid., **107**, p. 150, 1907.
[274] Chemist and Druggist, p. 178, 1904. J, Ind. Eng. Chem., **1**, p. 94, 1909.
[275] J. Am. Chem. Soc., **29**, p. 75, 1907. U. S. Dept. Agr., Bur. Chem., Bull., **105**, p. 23, 1907.
[276] Ibid., **132**, pp. 55–58, 1910.
[277] Francis H. Jennison: The Manufacture of Lake Pigments from Artificial Colors. London: Scott, Greenwood & Co., p. 73; 1910.
[278] Ibid., p. 74.

observed that a dyed clay is brilliant or dull according to the whiteness or darkness of the original clay. We consider the formation of a clay lake as truly that of a chemical compound as is the formation of a tannic-acid lake. Jennison also says: [279]

> The formation of lakes from basic colors is dependent on the combination of the amido or basic group or groups in the color molecule with various acids producing insoluble salts of the coloring matters.

If, then, the colloid-acid radicals of good colored clays are dissolved by suitable deflocculants, and decanted from the crystal sediments, they should give pure lakes on adding first the dye and then sufficient acid to neutralize the alkali bases present. The coagulum may be treated by usual methods to incorporate it with oil, etc.

28. PAINTS

Natural pigments, such as ochre or sticky hematite, for example, may be deflocculated, decanted from the gritty sediment, coagulated, and incorporated with oil. Such a process, by its avoidance of grinding, may prove of economic importance in paint manufacture.

Zachariah Cartwright [280] has a clearly conceived patent for preparing "solutions or pseudosolutions" of hydrated oxides, such as those of iron, manganese, chromium, and the like, ordinarily insoluble in water, consisting in mixing the finely powdered oxide with an aqueous solution of soap. The oxides are insoluble in solutions containing 10 per cent or more of soap. Around 5 per cent is a "critical" point; weaker solutions dissolve or suspend the oxide; 1 per cent and 0.5 per cent give solutions of great permanency. The permanency may be increased or the solution protected against excess of alkali by adding sugar, etc., to prevent precipitation. This solution may be used for dyeing fabrics, etc. "Fixing agents such as gum may be incorporated with the oxide solution and the latter may then be evaporated down to any required degree of concentration." The 1 per cent solution may be decanted from impurities, such "totally insoluble" substances as silica, etc., and then coagulated, preferably by acid, though excess of alkali may be used. When 5 per cent soap solution is used, there is obtained a temporary or "time

[279] Ibid., p. 79.

[280] British Patent 24842 (Nov. 18, 1908).

solution," from which everything is precipitated in two hours. In this case the impurities fall first, then the least hydrated oxides, and in succession, the more highly hydrated oxides. These form a distinct layer upon the impurities, and may be readily scraped off. As the colors of the hydrated iron oxide vary from deep red to light yellow with the degree of hydration, it is possible to match any desired sample by watching the progression of shades from dark red to yellow, interrupting the sedimentation and decanting when the color matches the sample. Seven per cent is the maximum amount of oxide that it is advisable to suspend, on account of impairing fluidity. After precipitating the decanted solution with acid, it is washed and dried, when it is ready for the market.

In conclusion, it would seem that the idea of the exchange of bases and the other ideas advocated in this paper might be of service in connection with questions of fertility and its dependence on the nature of the soil, the fertilizers used, etc. For instance, lime or any other reagent from a fertilizer might have the effect of putting into solution bases which are combined with the clay colloids; according to the composition of the resulting soil solution, the effect would be stimulating to vegetation or the reverse.

I. ACKNOWLEDGMENTS

In this investigation I have been very fortunate in having the unfailing support and helpful suggestions of my chief, Mr. A. V. Bleininger, and the hearty good will of my associates, especially Mr. W. E. Emley, who assisted me for some months, and Mr. S. E. Young, who spent a shorter period on the work.

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[281] Final revision of manuscript completed at this date.

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DEPARTMENT OF COMMERCE

TECHNOLOGIC PAPERS

OF THE

BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

No. 24

DETERMINATION OF PHOSPHORUS IN STEELS CONTAINING VANADIUM

BY

J. R. CAIN, Associate Chemist

and

F. H. TUCKER, Assistant Chemist

Bureau of Standards

[MAY 17, 1913]

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DETERMINATION OF PHOSPHORUS IN STEELS CONTAINING VANADIUM

By J. R. Cain and F. H. Tucker

It is known that vanadic acid, even when present in small quantity, interferes with the precipitation of phosphorus as phosphomolybdate. Where the quantity of phosphorus is small relatively to the vanadium, as in steel, the vanadium not only contaminates the precipitate which is obtained, but also retards the rate at which it is formed and may prevent complete precipitation.

While developing a method in this laboratory for the determination of vanadium by coprecipitation with phosphomolybdate,[1] it was observed that the vanadium is precipitated in this manner only when present in the quinquivalent condition; quadrivalent vanadium was not precipitated, neither was pervanadic acid. In some experiments made by adding enough hydrogen peroxide to a solution containing vanadium to convert all of it to the pervanadate, not the slightest coprecipitation was observed with large or small amounts of added phosphate. The precipitates of phosphomolybdate obtained had the normal canary-yellow color, in contrast to the orange-red tint of precipitates containing vanadium. Other tests also showed no vanadium in such precipitates.

These observations suggested the possibility of determining phosphorus in the presence of vanadium by converting the latter to pervanadic acid before adding the molybdate reagent. To test this question, determinations of phosphorus in the B. S. Vanadium Standard (No. 24), in the B. S. Chrome-Vanadium Standard (No. 30), and in some synthetic solutions containing varying proportions of iron, chromium and vanadium, were carried out by the alkalimetric method, except that the vanadium was

[1] Cain and Hostetter: B. S. Tech. Paper No. 8; J. Ind. and Eng. Chem., 4, p. 250; 1912.

converted, before precipitation of the phosphorus, to pervanadic acid by means of hydrogen peroxide. While this method yielded satisfactory results with the majority of the large number of samples tested, there were occasional irregularities which we were not able to eliminate. In cases where the method failed the precipitates were red, the results were low, and no further precipitate formed after a long period of time. In a series of determinations with a given sample faulty results occurred only occasionally. A great deal of work was done in trying to find the causes of these apparently accidental failures by varying the concentration, temperature, acidity, etc., of the solutions, but without success.

Apparently the trouble is due to a decomposition of the hydrogen peroxide and of the peroxidized vanadium before complete precipitation of the phosphorus takes place, and this decomposition is probably caused by the presence of one or more of the numerous catalyzers which decompose hydrogen peroxide. Owing to this fact and to the further objection that hydrogen peroxide also peroxidizes the molybdenum of the precipitant, thereby causing possible abnormalities in the action of the latter, it was decided to abandon this method for general work. It is quite possible, however, that correct results on a given sample may be obtained by making several determinations and eliminating from the average those which are evidently wrong when judged by the criteria above indicated.

Experiments which resulted in the discovery of a satisfactory method based on reduction of the vanadium to the quadrivalent condition were then begun. The fact that phosphorus may be quantitatively precipitated by the molybdate reagent when present with vanadium in this condition [2] has long been known. We have found that the difficulty in applying this principle to the analysis of steel arises from the fact that whereas original solution of the metal must be made in nitric acid, if the direct molybdate precipitation is to succeed, the presence of this acid complicates the reduction of the vanadium as the operation is ordinarily carried out. It has often been attempted to reduce vanadium to the

[2] Treadwell Kurz. Lehrbuch der Analy. Chem., pp. 227 and 228, 4th Ed., Vol. 2, 1907.

quadrivalent state by means of ferrous iron, but the statements in textbooks referring to this method indicate, directly or indirectly, that success has not been attained. Thus, Johnson [3] states, and gives results indicating that such reduction, as carried out in his experiments, did not give correct results for phosphorus. Brearley and Ibbottson [4] give determinations on two samples of ferrovanadium containing large amounts of phosphorus, where the vanadium had been reduced under conditions specified by them.

Whether or not the phosphorus content which they reported was correct can not be deduced from their statements, for this element was not determined by any other method known to give a correct result. It is equally impossible to decide from their experiments whether the vanadium was completely reduced at the time of precipitation. If it was not completely reduced (causing low results for phosphorus), there would have been produced a corresponding amount of the orange-colored precipitate which always forms in the presence of vanadic acid, but this, when associated with the large amount of normal phosphomolybdate which they obtained (their samples contained 0.65 per cent and 1.35 per cent phosphorus, respectively), might easily have escaped their notice. From other statements made by Brearley and Ibbottson on this subject [5] it would appear that they believe the formation of an orange-colored precipitate has little significance in affecting phosphorus results, the deficiency in phosphorus precipitated in such cases being compensated by the positive error caused by the vanadium associated with the precipitate. In this connection it may be stated that our results show that formation of a red or orange-colored phosphomolybdate always indicates incomplete precipitation of the phosphorus.

Having confirmed, by a series of results, the fact that phosphorus is quantitatively precipitated as phosphomolybdate in the presence of quadrivalent vanadium alone, the disturbing factors operating when vanadic acid is reduced by ferrous iron in nitric-acid solutions of steels as a preliminary to the determination of phosphorus were investigated.

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[3] Chemical Analysis of Special Steels, etc., pp. 22 and 23; 1909.
[4] The Analysis of Steel Works Materials, p. 166; 1902.
[5] Loc. cit., p. 165.

Duplicate nitric-acid solutions of steel containing added vanadic acid were reduced with excess of ferrous sulphate. To one of the pair there was added the usual proportion of ammonia used in a regular phosphorus determination, and, after cooling, the color of the solution was compared with the companion solution to which no ammonia had been added. Not only had the blue color of the first solution due to reduced vanadium disappeared, being replaced by the yellow tint of vanadic acid, but the treated solutions usually gave but a slight test for ferrous iron. It thus appears that quadrivalent vanadium is oxidized by the nitric acid when the solution is heated by adding the necessary amount of ammonia. The vanadic acid thus formed would have prevented complete precipitation of phosphorus; moreover, most of the excess of ferrous iron, which would have tended to keep the vanadium reduced, had disappeared.

Solutions of steel containing vanadium and phosphorus were then prepared for precipitation of the latter by reducing with ferrous sulphate under the proper conditions to insure an excess of the reducing agent being present at the time of adding the molybdic reagent. When precipitation was made at 35° to 45° C, the solutions usually gave no test for ferrous iron after completion of the five-minute period of shaking generally recommended. When the reducing agent had thus disappeared, the oxidation of the hypovanadic acid was indicated by change in color of the solution, by abnormal color of the precipitate, and by low results. However, if precipitation was made at 15° C, excess of ferrous iron was almost always present.

We sought to determine whether phosphorus may be quantitatively precipitated as phosphomolybdate at low temperatures. With prolonged and thorough shaking or agitation of the solution, quantitative precipitation can be made at temperatures of 15° to 20° C, and our successful determinations, given in Table I, have been made at these temperatures. A 10-minute shaking suffices; the precipitate thus formed settles rapidly and filters as readily as that formed at 35° to 45° C in the ordinary procedure for determining phosphorus in steels.

Even with an excess of ferrous iron, as indicated by the ferricyanide drop test, red or orange-colored precipitates and low

results were often obtained. The solutions in such cases had a deep red color. There was a strong odor of oxides of nitrogen and sometimes even evolution of these gases. It was evident, then, that under certain conditions vanadic acid in nitric acid solution would not be completely reduced by ferrous iron, even with a considerable excess of the latter present. The trouble was found to be caused by the presence of oxides of nitrogen, due to interaction of ferrous iron and nitric acid; for when the gases were expelled from the solution, for instance by passing carbon dioxide in the cold for a sufficient time, the deep red color disappeared, the phosphorus precipitates were normal in color, and the results were quantitatively correct. To further test this point, a vanadate solution was reduced by sulphurous acid, the excess of reducer removed, and the vanadyl solution thus formed added to the nitric-acid solution of a vanadium-free steel. Oxides of nitrogen, formed during the solution of zinc in nitric acid, were passed into the solution thus prepared. A gradual disappearance of the blue color, due to reduced vanadium, was observed, and the phosphomolybdate precipitate obtained from the solution of the steel was orange colored, both results indicating that the oxides of nitrogen had caused oxidation of the vanadium. Some experiments were also made by precipitating phosphorus from steels containing vanadium, by reducing the latter with an excess of ferrous sulphate, the flask in which precipitation was made being filled with carbon dioxide; under these conditions there was complete precipitation and the phosphomolybdate had the normal color. It thus appears probable that the nitric oxide (NO) formed by action of the ferrous salt on nitric acid serves as a carrier of atmospheric oxygen to the vanadyl compound.

The method of preparing solutions of steels for phosphorus determination in the experiments described above was the usual one of dissolving in nitric acid of 1.135 specific gravity, oxidizing with excess of permanganate solution, and destroying the excess of oxidizer (with simultaneous partial or complete reduction of the chromic and vanadic acids in solution) by ferrous sulphate, sulphurous acid, or a sulphite. After the observations above noted had been made, it was finally found that, observing the

precautions shown to be necessary by the preceding experiments, samples in which the preliminary reductions of excess of permanganate, manganese dioxide, etc., were made with ferrous sulphate almost always gave trouble through incomplete precipitation, red or orange-colored precipitates, etc., whereas, on the other hand, samples in which this reduction was made by sulphurous acid or a sulphite nearly always gave good results. In the latter class of samples, also, after addition of ferrous sulphate to complete the reduction of the vanadium before adding the molybdate reagent, no odor of nitrous fumes was noticeable. Experiments were then made with the idea of reducing the vanadium by sulphurous acid alone, without the use of ferrous salt at all. This can be done; the essential conditions are to keep the temperature of the solution low and to allow time enough. Phosphomolybdate precipitated from such solutions has the normal color, and precipitation is quantitative. On account of the long time necessary, however, reduction by sulphurous acid alone is not to be recommended for routine work.

Our conclusion, then, is that the presence of small amounts of sulphurous acid in the solutions where that reagent was used as a reducing agent for destroying permanganate, etc., counteracted the effect of, or prevented the formation of, oxides of nitrogen upon adding ferrous salt. The formation of these oxides being thus avoided, their effect in preventing complete reduction of vanadic acid by ferrous salt was eliminated, and hence correct results could be obtained for phosphorus.

As a result of these investigations, then, the following four conditions should be observed in precipitating phosphomolybdate in nitric-acid solutions of steels containing vanadium by the method of reduction of the vanadium to the quadrivalent state:

(1) The temperature of precipitation should be held at a point (15° to 20°) where the nitric acid does not oxidize the excess of ferrous salt or the reduced vanadium before complete precipitation of phosphorus takes place; (2) the partial neutralization with ammonia, frequently used when phosphorus is precipitated as phosphomolybdate, must be made before reduction of the vanadic acid, otherwise the heat of neutralization causes reoxidation of most of the ferrous iron and reduced vanadium by the nitric acid;

(3) care must be taken to prevent the action of oxides of nitrogen, formed by interaction of ferrous salt and nitric acid, on the reduced vanadium; since these substances seem to catalyze the oxidation of the vanadyl salt and may in some cases completely prevent precipitation of the phosphorus, owing to the large amount of vanadic acid so produced; (4) efficient means for shaking or agitation of the solutions in which precipitation is to take place must be provided. A fifth condition, not likely, however, to give trouble with ordinary care, is the avoidance of too great an excess of ferrous salt. Under certain conditions, not fully investigated by us, a large excess of ferrous iron in the presence of vanadic and molybdic acids causes reduction of the latter, which, of course, is to be avoided for the present purpose. When all these conditions are observed there is no coprecipitation of vanadium in solutions containing as high as 1.5 per cent of this element. This point was verified by testing phosphomolybdate precipitates (from a steel containing 0.112 per cent phosphorus and 1.5 per cent vanadium) for vanadium by dissolving the precipitates in concentrated sulphuric acid, adding a drop or two of nitric acid and heating till fumes were given off strongly; on cooling no yellow color developed, showing that no vanadium had been coprecipitated.[6]

The method, which is described below, is adapted to any steel containing vanadium, no other element which ordinarily complicates the determination of phosphorus being present. If tungsten, titanium, arsenic, tin, etc., are present, their disturbing influence is eliminated by the usual methods for steels containing no vanadium. Nickel, copper, chromium, molybdenum, or aluminum, when present as alloying elements along with the vanadium, do not interfere. The details of the method are as follows: The solution of the steel, up to the point where precipitation of the phosphorus is to be made, is prepared as for an ordinary phosphorus determination by the alkalimetric method, viz, solution of 1 to 2 grams in 100 cc of nitric acid (specific gravity 1.135), oxidation with slight excess of permanganate solution while boiling, destruction of the excess of permanganate, etc., by a slight excess of sulphur dioxide or a sulphite, cooling of the solution

[6] Cain and Hostetter, loc. cit.

and addition of 40 cc of ammonia (specific gravity 0.96). Any steel which does not give all its phosphorus to the solution by this method must be treated in an appropriate manner, so that the acidity, concentration of ammonium nitrate, and total volume obtained are always the same as by the method of solution directed. Slight deviations from these conditions are, however, probably without significance. Assuming solution of the steel and partial neutralization to have been made as directed, the solution is cooled to 15° to 20° C, and 5 cc of a saturated solution of ferrous sulphate and two to three drops of concentrated sulphurous acid are added. After addition of 40 cc of molybdate reagent the solution is shaken in an efficient manner for 10 minutes. The precipitate, after settling (which is quite rapid), is then filtered off, washed in the usual manner, and titrated by the alkalimetric method.

The following table gives results by this method on synthetic solutions made with B. S. standard acid open-hearth, basic open hearth, and Bessemer steels, of varying phosphorus and carbon content, to which vanadium was added as sodium vanadate and chromium as chromium nitrate. The acid and alkali solutions used for titrations were standardized against B. S. standard steels No. 19a (A. o. H. 0.2) and No. 9a (Bes. 0.2 renewal). The individual determinations in each series are single determinations only; the good agreement in all cases with the certificate values for phosphorus of the individual steels shows the reliability and accuracy of the method.

TABLE 1

B. S. steel standards	Vanadium present, per cent approximately	Chromium present, per cent approximately	Phosphorus present, per cent (certificate value)	Phosphorus found with—		Differences (in percentages on steel) with—	
				V. present	V.+Cr. present	V. present	V.+Cr. present
V. steel No. 29	[7] 0.15	.....	0.035	0.037	.....	+0.002	.....
	[7] .15	.....	.....	.038	.....	+ .003	.....
Cr. V. steel No. 30	[7] .21	[7] 1.35	.043	.....	0.046	.....	+0.003
	[7] .21	[7] 1.35	.....	.....	.048	.....	+ .005
B. O. H. 0.2 C. Renewal 11a	.2	.5	.0082	.007	.008	− .001	− .000
	.4	1.0	.....	.008	.007	− .000	− .001
	.6	2.0	.....	.008	.006	− .000	− .002
	.8	3.0	.....	.008	.010	− .000	+ .002
	1.0	4.0	.....	.007	.008	− .001	− .000
B. O. H. 0.8 C. Renewal 14a	.2	.5	.0246	.024	.023	− .001	− .002
	.4	1.0	.....	.025	.022	+ .000	− .003
	.6	2.0	.....	.024	.024	− .001	− .001
	.8	3.0	.....	.023	.024	− .002	− .001
	1.0	4.0	.....	.023	.022	− .002	− .003
B. O. H. 1.0 C. Renewal 16a	.2	.5	.045	.044	.046	− .001	+ .001
	.4	1.0	.....	.046	.047	+ .001	+ .002
	.6	2.0	.....	.044	.047	− .001	+ .002
	.8	3.0	.....	.046	.050	+ .001	+ .005
	1.0	4.0	.....	.049	.044	+ .004	− .001
A. O. H. 0.2 C. Renewal 19a	.2	.5	.084	.087	.085	+ .003	+ .001
	.4	1.0	.....	.084	.083	.000	− .001
	.6	2.0	.....	.084	.083	.000	− .001
	.8	3.0	.....	.086	.084	+ .002	.000
	1.0	4.0	.....	.084	.083	.000	− .001
B. O. H. 0.2 C. Renewal 9a	.2	.5	.112	.106	.109	− .006	− .003
	.4	1.0	.....	.111	.117	− .001	+ .005
	.6	2.0	.....	.111	.109	− .001	− .003
	.8	3.0	.....	.110	.116	− .002	+ .004
	1.0	4.0	.....	.106	.106	− .006	− .006

[7] Certificate values.

The time required is practically that for determining phosphorus in an ordinary steel.

WASHINGTON, May 17, 1913.

DEPARTMENT OF COMMERCE

TECHNOLOGIC PAPERS

OF THE

BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

No. 25

ELECTROLYTIC CORROSION OF IRON IN SOILS

BY

BURTON McCOLLUM, Associate Physicist

and

K. H. LOGAN, Assistant Physicist

Bureau of Standards

[JUNE 12, 1913]

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ELECTROLYTIC CORROSION OF IRON IN SOILS

By Burton McCollum and K. H. Logan

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I. INTRODUCTION

The term "electrolytic corrosion" is most frequently used to indicate corrosion caused by the discharge of an electric current which enters the metal from external sources. During recent years, however, the theory has been widely accepted that all corrosion in water solutions is essentially electrolytic in its nature,

and in consequence there have come into use a variety of terms such as "galvanic action," "stray current electrolysis," "self-corrosion," etc., to distinguish between the cases of corrosion originating from different causes. Thus, corrosion of buried iron may be due to galvanic action caused by physical or chemical differences between adjacent points on the surface of the metal, to the presence of foreign substances in the soil, such as coke cinders, iron oxides, etc., which set up local galvanic action, or it may be due to the discharge of electric currents that have entered the structure at some remote point. In the present paper the terms "electrolysis" and "electrolytic corrosion" are used to designate corrosion caused by the discharge of electric current which has entered the metal from some outside source, while all other forms of corrosion in which the electric currents originate within the corroding system itself from whatever cause are referred to as "self-corrosion." It should be pointed out at the outset, however, that these two general classes of corrosion are by no means independent of each other, since the presence of either kind of corrosion generally affects in marked degree the nature and extent of the other under a given set of conditions. This mutual influence is such as to be of considerable practical importance, and in particular it often greatly increases the difficulty of obtaining trustworthy experimental data in regard to electrolytic corrosion proper.

The data herein presented represent a portion of the work done by the Bureau of Standards in connection with a more general investigation of the subject of electrolysis and electrolysis mitigation, which has been in progress for some time past. The present paper is designed to deal only with the fundamental laws governing electrolytic corrosion under practical conditions, and relates to self-corrosion only in so far as it is necessary to distinguish between the two classes. The subject of the prevention of electrolytic damage is referred to only incidentally, when occasion requires, in order to interpret the significance of results obtained. This matter of electrolysis prevention has been given much attention and will be treated at some length in a report which will be issued shortly by the Bureau of Standards, dealing exclusively with the subject of electrolysis mitigation.

In studying the phenomena of electrolytic corrosion in soils under practical conditions many variables are encountered which tend in greater or less degree to affect the results. Among these may be mentioned the current density at the surface of the metal, the moisture content of the soil, the presence of oxygen either in the gaseous state or dissolved in soil waters. The latter not only affects the rate of corrosion but also affects the character of the end products of the reactions, and thus to some extent has a bearing on the question of diagnosing the cause of particular cases of corrosion. The temperature of the soil is also important, particularly because of its effect on the current flow. In the case of iron, the formation of oxids as a result of the initial corrosion may complicate matters because of their possible action in stimulating galvanic action. Other factors, such as the mechanical and chemical properties of the soil, the depth of burial of the metal, the limitation of current flow due to polarization, the formation of high resistance films on the surface of the metal, and the pitting of the surface, due to a variety of causes, may likewise act to increase or decrease the rate at which damage may progress, and therefore require special investigation. Finally, since it is not practicable to carry on all experiments in the field under practical conditions, it is necessary to study the possible differences in results that may in some cases occur between experiments performed in the laboratory and in the field. It is these factors that are dealt with in the following pages, and while the investigations have in most cases not yet been completed, we believe that the data thus far obtained will be of sufficient interest to justify a report of progress at this time.

While the corrosion of iron by electric currents may be influenced by a variety of causes, the data to be presented later show that under most practical conditions the extent of the corrosion is to a large extent a function of the quantity of electricity that is discharged from a given surface. This is a quantity that can be readily measured under laboratory conditions and we have therefore determined, in all cases, the corrosion as a function of the ampere-hour discharge from the anode. The results are expressed in terms of the "corrosion efficiency." If the corrosion of the

anode is the sole reaction involved at the anode, then, according to Faraday's law, 96 540 coulombs are required to corrode 1 gram equivalent of the metal and the corrosion efficiency is said to be 100 per cent. In most cases, however, the actual corrosion noted is either greater or less than this amount, and the percentage which the actual corrosion in any case is of the theoretical amount may be called the "efficiency of electrolytic corrosion," or more briefly, "corrosion efficiency," under those conditions. The experimental data presented in the first part of this paper show how the efficiency of corrosion is affected by the varying physical conditions encountered in practice.

The corrosion efficiencies are in all cases calculated on the assumption that the iron is divalent. The experiments presented show that in most cases at least this was true, since, as a rule, the corrosion efficiencies observed have been near or above 100 per cent. This is therefore the logical basis on which to figure the efficiency of corrosion. In those cases where the corrosion efficiency was very low it may be due in part to the iron taking the ferric state, and such tendency, when it exists, may therefore be regarded as one of a number of possible causes of low efficiency of corrosion. The various factors enumerated above which affect the efficiency of corrosion of iron in soils are discussed in detail in a later part of this paper.

1. ARRANGEMENT OF APPARATUS

The methods of conducting the experiments recorded below were, in general, the same, and may therefore be described once for all.

The local earths used in the laboratory tests were from virgin soil near the laboratory, sifted to remove stones and to insure uniformity. This earth was mixed with the desired amount of distilled water and placed in tin cans, which served as cathodes. The bottoms of the cans were separated from the earth by a thick layer of paraffin or other insulating material, so that the discharge from the anode placed in the center of the can would be substantially uniform and only toward the sides of the can. The outside of the cans were insulated from each other by several layers of heavy paraffined paper. In a number of experiments,

however, the test specimens were buried in virgin soil out of doors in order to compare directly the corrosion found under these conditions with the corrosion which resulted when the tests were made in the laboratory.

2. CLEANING OF ANODES

In cleaning the anodes and determining their losses, a number of precautions are necessary. It has been shown that many solutions render iron at least temporarily passive. Such solutions are, of course, not desirable for cleaning iron previous to a test. The iron used was filed and sandpapered to remove dirt and scale, cut into suitable lengths, stamped on one end with steel numbers for identification, and weighed. Rubber-covered leads were then soldered to the unnumbered ends of the anodes and both ends covered with paraffin or pitch. To make these stick to the iron it is necessary that it should be rather hot when they are applied. The specimens were then thoroughly washed with gasoline to remove any grease due to handling and finally dried with a towel. At the close of the experiment the specimens were washed and brushed to remove all loose dirt and then made cathode in a 2 per cent solution of sulphuric acid with a high-current density. To prevent plating a noncorrodable anode should be used. This method of cleaning was developed after various mechanical and chemical methods had been tried with inconsistent results and has proven very satisfactory.* The specimens came from the solution perfectly clean within 10 to 30 minutes and careful tests have shown that clean iron subjected to the treatment suffers no loss. The method seems very much preferable to any mechanical method we have tried, since when the rust sticks very tightly or the iron is rough it is impossible to remove the corrosion products without scraping off some of the iron with them. In a few instances where it was not convenient to clean the iron electrolytically, as in the case of hollow anodes too small to permit the interior to be protected by inserting an anode, a solution of ammonium citrate has been used. This latter method is satisfactory, except in the case of deep pits, especially if a warm solution is used.

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* For cleaning wrought iron and steel.

NOTE.—Cast-iron specimens should not be cleaned electrolytically with an acid electrolyte after a corrosion experiment, as the acid attacks the iron. An alkali solution may be substituted for final cleaning, but the alkali may render the iron passive, and so is unsuitable for use before a test. Electrolytic cleaning with alkali electrolytes is not as rapid or satisfactory as with acid. The ammonium citrate solution is recommended for small specimens of cast iron.

The paraffine protecting the ends of the specimens was removed by gasoline and the pitch by toluol. The solder attaching the leads was melted and carefully wiped off. We have also tried dissolving the solder by mercury, but the process is slow unless heat is used, and the result no better than the easier method.

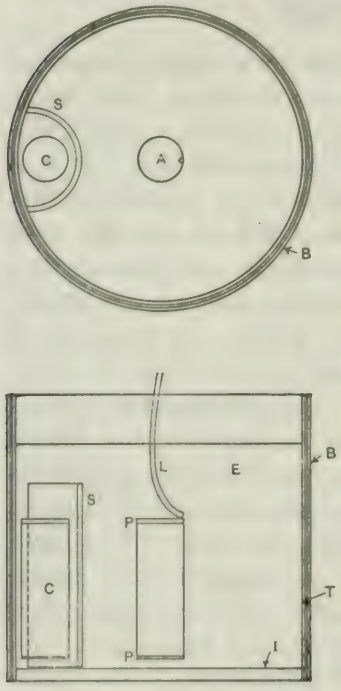

Fig. 1.—*Showing arrangement of apparatus for corrosion tests*

A, anode; T, containing vessel; B, insulation; I, insulating bottom; P, paraffin coating on ends of anodes; L, lead; C, check specimen; S, insulating shield

3. CHECK SPECIMENS

Correction for the loss by the anodes due to self-corrosion was made by placing a check specimen inside each can and screening it from the anode by a shield of glass or paraffined paper. Fig. 1 shows the arrangement of the anode and check specimen. The loss of this check specimen has been deducted from the loss of the anode and the difference used as the loss due to electrolysis. It will be shown later that the loss of check specimen in a can with an anode is considerably greater than that of a similar check specimen in a separate vessel of the same earth and it seems therefore that part of the loss in the former case is due to some effect of the current and should be charged against it. The corrosion efficiencies found are consequently lower than if check specimens in separate cans were used. However there are several advantages in keeping the check specimen in the can with the anode and the increased loss on this account is usually small compared with the total loss of the anode.

4. DETERMINATION OF AMPERE HOURS

To obtain the corrosion efficiency it is of course necessary not only to determine accurately the loss of the anode, but equally essential to know the quantity of electricity discharged by it. To

obtain this the specimens were so arranged that the current could be read at frequent intervals, compensation being provided where necessary for the resistance of the milliammeter. Curves were plotted showing the relation between the current and time, and the area between the curve and the axes determined with a planimeter. While the exact current values between times of observation are unknown, the areas represent a value of the ampere hours sufficiently accurate for practical purposes, and the large number of circuits operating at one time made the use of more accurate recording instruments out of the question.

II. FACTORS AFFECTING EFFICIENCY OF CORROSION

1. EFFECT OF CURRENT DENSITY

A number of investigators have reported experiments showing that the amount of corrosion which results from a given ampere hour discharge varies greatly from the theoretical amount. Among these may be mentioned the work of Hayden,[1] and of W. W. Haldane Gee,[2] who worked with high current densities, and observed that there was a marked tendency for the iron to become passive, the resulting corrosion being considerably less than the theoretical amount. In general this tendency toward passivity was much more marked when the current density was very high. These experiments were carried out with test specimens immersed in liquid baths, however, so that the conditions were very different from those which prevail in ordinary street soils. Ganz[3] has reported the results of experiments carried out in certain soils, which showed that the actual corrosion observed was much greater than the theoretical amount, in some cases the loss in weight being as much as several times the loss calculated from Faraday's law. In these experiments very low current densities were used and the earth contained considerable quantities of salt, and this may have affected the result. The authors have carried out several series of experiments in which the aim has been to maintain conditions as nearly as possible approximating those which will be encountered in practice, both as regards soil conditions and cur-

[1] Jour. Franklin Inst., Vol. 172, p. 295.
[2] Jour. Municipal School of Tech., Manchester, Vol. 2, 1910.
[3] Proc. A. I. E. E., June, 1912, pp. 1001–1010.

rent densities. The soil used was a virgin soil taken from a sparsely settled portion of the residential district of Washington. An analysis was made of a typical sample of the soil for those ingredients which are most likely to affect corrosion, the results being shown at the top of Table 1 along with the data on efficiency of corrosion.

In determining the current densities to be used values were chosen of such magnitude as could give rise to considerable injury within a period varying from a few months to 15 or 20 years. For example, the highest value used was about 5 milliamperes per square centimeter, which under uniform distribution and at 100 per cent efficiency of corrosion would cause the corrosion to progress inward at the rate of about 5.7 centimeters per year, which corresponds to a rate rarely exceeded under practical conditions. The minimum current density used was 0.05 milliamperes per square centimeter, which corresponds to a normal rate of corrosion of about 1 centimeter in 17 years. These extreme ranges represent therefore the limits between which the corrosion is of much practical importance.

Several series of experiments were made, the data presented in Tables 1 and 1a being typical of the series. The corrosion efficiencies under Table 1 are for a soil containing considerably less moisture than those under Table 1a, which are obtained on a soil practically saturated with water. In the former the test specimens were all imbedded in samples of earth placed in tin cans as described above, while in the second series half of the tests were run with specimens buried to a depth of about 2½ feet in the ground out of doors.

The data in Table 1 are plotted in Fig. 2, and those of Table 1 a are plotted in Figs. 3 and 4, the curve of Fig. 4 being a continuation of that of Fig. 3, but on a smaller scale. While the points do not lie on a smooth curve, because of a number of disturbing factors to be discussed later, the trend of the curves is nevertheless unmistakable. They show corrosion efficiencies varying greatly with the current density, the ranges being from about 20 to 140 per cent for the range of current density varying from about 5.0 to 0.05 milliamperes per square centimeter, the lower

corrosion efficiencies being obtained at the higher current densities. All of the data in Tables 1 and 1 a are plotted as a single curve in Fig. 5, which, in spite of the irregularities in the individual points shows clearly the decided falling off in efficiency of corro-

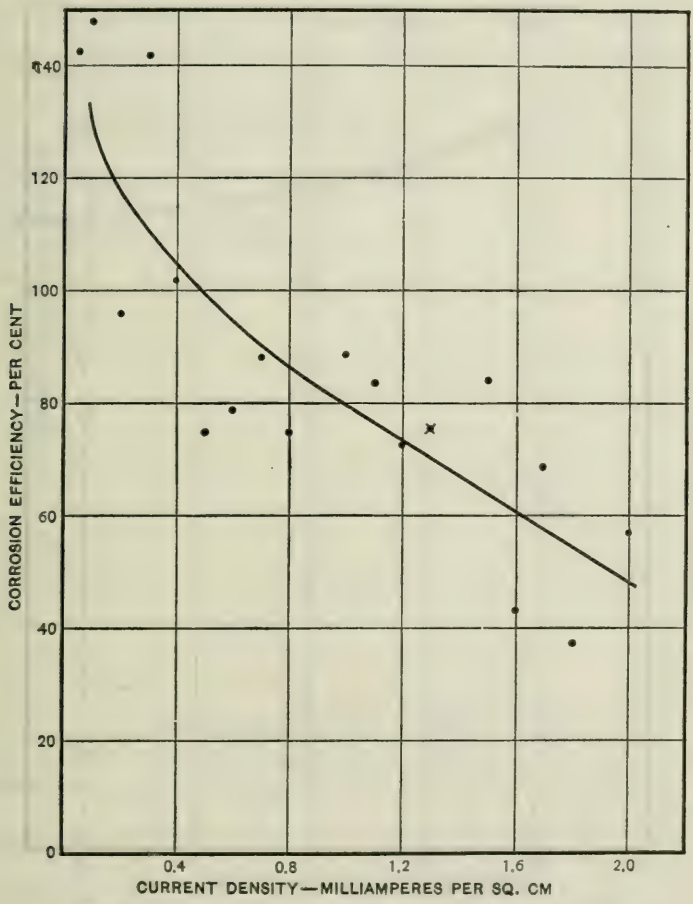

Fig. 2.—*Effect of Current Density on Efficiency of Corrosion*

sion with increase in current density. It is interesting to note here that the points in Fig. 5 marked with an x were taken out of doors in native earth while those marked with dots and circles were two separate series taken indoors, using small samples of earth in cans. The agreement between the different groups is

fully as good as that between different points of the same group which indicates that the results obtained on small samples in the laboratory are substantially the same as those obtained on specimens buried in the earth out of doors. This gradual change

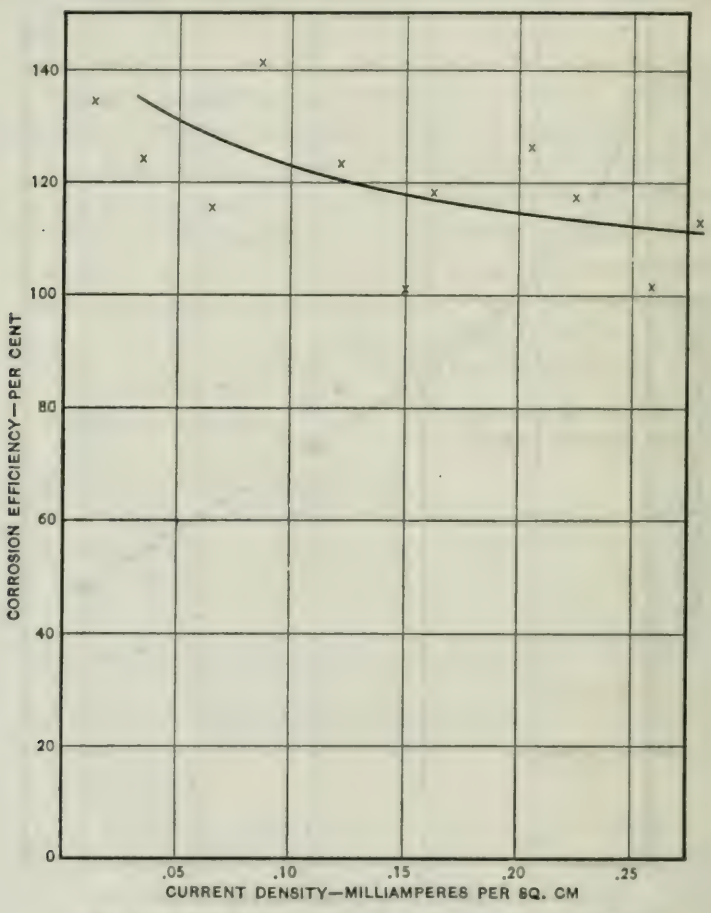

Fig. 3.—*Effect of Current Density on Efficiency of Corrosion*

in corrosion efficiency with current density does not appear in accord with the results of Hayden, Haldane Gee, and others, whose work with liquid electrolytes seemed to indicate an abrupt change in efficiency of corrosion from 100 per cent to zero at a critical current density.

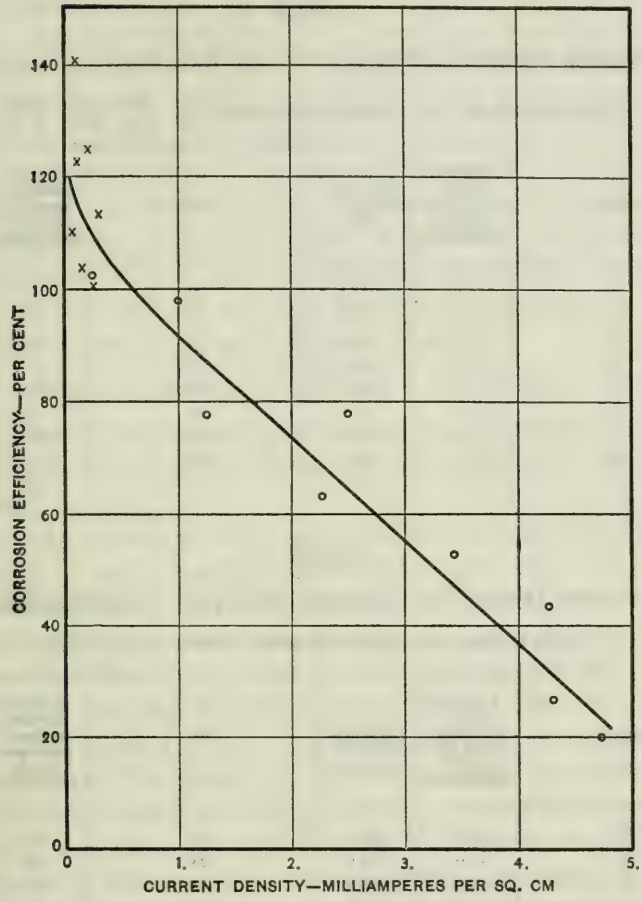

Fig. 4.—*Effect of Current Density on Efficiency of Corrosion*

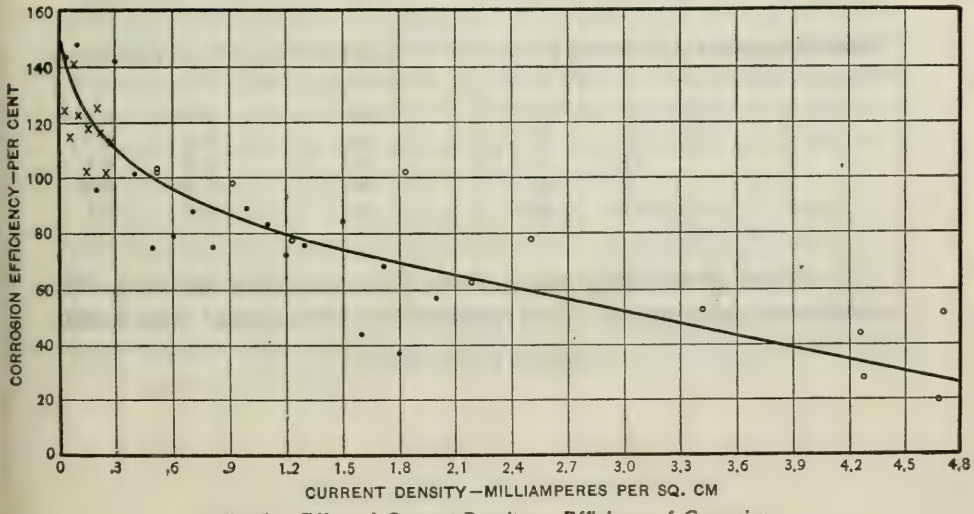

Fig. 5.—*Effect of Current Density on Efficiency of Corrosion*

TABLE 1

Relation between Current Density and Efficiency of Corrosion

[Partial analysis, per cent of moisture-free sample $\frac{Cl}{0.002}$ $\frac{NO_2}{0.002}$ $\frac{CO_3}{0.003}$ $\frac{SO_4}{0.004}$]

No.	Density, milliamperes per square centimeter	Efficiency of corrosion	No.	Density, milliamperes per square centimeter	Efficiency of corrosion
1	2.0	57.6	10	.8	75.0
2	1.8	37.4	11	.7	88.3
3	1.7	69.2	12	.6	79.1
4	1.6	43.2	13	.5	75.2
5	1.5	84.3	14	.4	102.1
6	1.3	75.8	15	.3	142.2
7	1.2	72.9	16	.2	96.2
8	1.1	83.8	17	.1	148.4
9	1.0	89.2	18	.05	142.9

TABLE 1 a

Current Density and Corrosion Efficiency—Outdoor Tests

[Area of anodes 70.9 square centimeters. Time of run, 115 hours]

No.	Current density, milliamperes per square centimeter	Corrosion efficiency	No.	Current density, milliamperes per square centimeter	Corrosion efficiency
19	0.034	124.1	24	.163	118.3
20	.064	115.0	25	.206	125.8
21	.088	141.5	26	.222	117.1
22	.129	123.6	27	.258	101.8
23	150	104.6	28	.279	113.4

[2-hour run in saturated soil in laboratory 4–27–13 to 4–30–13. Exposed anode area 11.78 square centimeters]

29	0.48	102.5	34	2.50	78.1
30	1.01	98.1	35	3.45	52.9
31	1.26	78.3	36	4.27	43.6
32	1.84	102.2	37	4.29	27.4
33	2.28	63.6	38	4.72	20.4

It will be noted that these results do not show as high efficiencies of corrosion as those reported by Prof. Ganz,[4] who found

[4] Proc. AI. E. E., June, 1912.

values ranging over 500 per cent. It should be noted, however, that the results obtained by Prof. Ganz were for the most part obtained on much lower current densities than were used in the present experiments. It is seen also from Fig. 5 that as the lower current densities are approached the curve tends rather strongly upward, indicating that if the current density had been reduced to the low value used by Ganz the corrosion efficiencies might have reached the high values found by him. As pointed out above, however, lower current densities than those used in the present series, although of great theoretical interest, are of little consequence from the practical standpoint.

2. EFFECT OF MOISTURE ON THE RATE OF CORROSION

The following experiments were tried to determine whether the amount of moisture in the soil affected the corrosion efficiency of iron buried in it.

A quantity of red clay soil was air dried and then distilled water was added, a can of earth taken out, more water added, etc., till six cans of earth had been obtained.

The ends of the specimens and the bottom and outside of the cans were insulated as in previous tests and small dishes of water placed inside the can to retard evaporation. The six cans were connected in series, the sides of the cans serving as cathodes and a current of 10 milliamperes giving about 1 milliampere per square centimeter was maintained by daily adjustments for 18 days. At the end of this time the resistance had increased so much that it was difficult to maintain the current and the specimens were therefore removed, cleaned, and weighed. The efficiency of corrosion was then computed, corrections being made for self-corrosion.

While the current was flowing, samples of the earth taken when the specimens were placed in the cans were dried for about a week in an oven at a temperature of 105° and the percentage of moisture computed from the loss of weight. The per cent of moisture is expressed in terms of the earth before drying.

The experiment was repeated, using 12 samples of earth. In order to run the entire set in series it was necessary to use a current of 2 milliamperes instead of 10 milliamperes as in the first trial. This may account for the difference in the results obtained in the two series. The methods were the same in each case. The

results of these tests are given in Table 2 and those for the second series are plotted in Fig. 6.

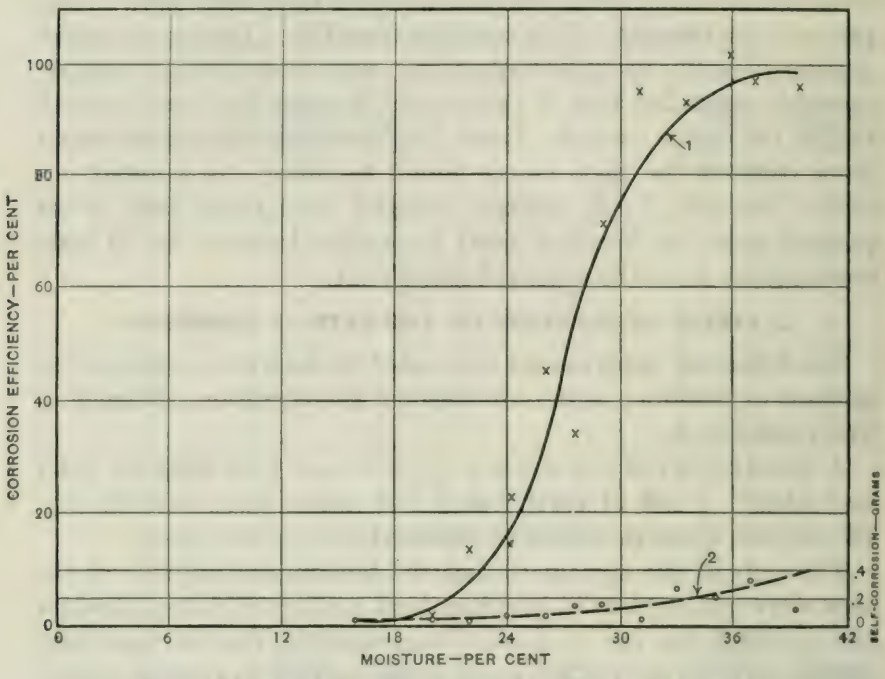

Fig. 6.—*Effect of Moisture Content of Soil on Efficiency of Corrosion*

TABLE 2

Effect of Moisture on Corrosion

No.	Per cent moisture	Loss in grams			Per cent efficiency of corrosion
		Total	Self-corrosion	Electrical corrosion	
1	15.9	0.090	0.044	0.046	1.1
2	20.0	.110	.040	.070	1.6
3	22.5	.623	.039	.584	13.7
4	23.8	.715	.080	.635	14.9
5	26.0	2.002	.073	1.929	45.3
6	27.6	1.579	.145	1.434	33.7
7	28.9	3.192	.160	3.032	71.2
8	31.1	4.182	.121	4.061	95.4
9	33.3	4.217	.265	3.952	92.8
10	35.7	4.545	.207	4.338	101.9
11	37.0	4.463	.335	4.132	97.0
12	39.4	4.218	.125	4.093	96.2

Looking at the curves of self and electrolytic corrosion, it will be seen that where a point on one curve is too high, the corresponding point on the other curve is too low. Since the electrolytic curve was obtained after natural losses had been deducted it is evident that some of the irregularities are due to incorrect values of the natural loss. However, the natural loss is so small that in most cases it could not account for the entire variation in the electrolytic curve. Since all wrought iron contains more or less slag, it is probable that the presence of minute slag particles explains, in part at least, the pitting and variations of results from expected values.

The results of these tests show that the corrosion efficiency varies greatly with the moisture content of the soil, being so small as to be practically negligible when the soil is fairly dry, but approaching values of the order of 100 per cent when the soil becomes saturated. In these tests there was very little corrosion when the moisture content was below 20 per cent. It should not be assumed, however, that the numerical values given here will hold for all soils, since there is considerable uncertainty as to the conditions which actually prevail.

In the first place, the percentage of moisture required to produce a wet condition of the soil varies greatly with different soils so that the percentage of moisture can not be taken as a measure of the condition of dryness. In the red-clay soil used in these tests the soil appeared to be barely moist at 15 or 20 per cent moisture, whereas we have since encountered numerous soils in which 10 per cent of moisture caused it to appear quite wet. There may also be variations due to differences in soil composition which affect the efficiency of corrosion. Further, while the average current density in these experiments was maintained practically constant it is not improbable that the actual current density varied considerably. When the soil is practically saturated with water the current density is probably nearly uniform, but as the moisture content is reduced and some of the pores in the soil become voids, there is a tendency for the current to discharge locally at the points of contact between earth and iron, and it appears possible that this may give rise to great variation in the actual current density of the discharge. It has already been seen

that at high current densities the efficiencies of corrosion tend to become smaller, so that the variations in efficiency of corrosion here observed as due to changes in moisture content may after all be due in large part to changes in current density. However this may be, the important fact is that the amount of corrosion per ampere hour is likely to be quite low in the case of fairly dry soils, while as the percentage of moisture approaches that corresponding to saturation the corrosion efficiency approaches 100 per cent for the particular value of current density used in this series, namely, 1 milliampere per square centimeter.

3. EFFECTS OF TEMPERATURE

In order to study the effects of temperature on the efficiency of corrosion of iron in soil, three series of experiments were carried out. In the first of these the temperature of the cans containing the earth samples was maintained practically constant at between zero and 1° C by means of an ice bath; the second was run at between 24° and 27° C, which corresponds to about average summer temperature in soils; and the third group was maintained at between 35° and 40° C by means of an automatically regulated oven. Four specimens were used in each group, and the current density was maintained practically constant at about 0.84 milliamperes per square centimeter.

The tests were all run in the same kind of earth, which was kept practically saturated with moisture. The results of these tests are given in Table 3. An examination of the values of efficiency of corrosion will show that they are practically independent of the temperature. It appears, therefore, that it is safe to assume that throughout the range of temperatures that are likely to be encountered under practical conditions temperature variations have no marked effect on the corrosion efficiency of iron in soils. This does not mean, however, that temperature is not an important factor in electrolysis under practical conditions, for the reverse is true; but this grows out of the effect of temperature on the resistance of the soil rather than on the efficiency of corrosion. It is shown in a later part of this paper that the resistance of soils varies with temperature in a very remarkable manner even within the ranges of temperature that are likely to occur in soils under

ordinary conditions, and that the effect of this change in resistance on the current flow is such as to make the actual amount of electrolysis which may be expected vary greatly with temperature. This matter is discussed later under the head of earth resistance.

TABLE 3

Effect of Temperature on Corrosion Efficiency

[Average current density, 0.84 milliamperes/cm²]

No.	Temperature	Corrosion efficiency
1	35 to 40° C.	98.2
2		103.4
3		97.0
4		98.4
	Average	99.2
5	24 to 27° C.	98.2
6		97.6
7		97.9
8		97.6
	Average	97.8
9	0 to 1° C.	93.8
10		95.7
11		99.1
	Average	96.2

4. EFFECT OF DEPTH OF BURIAL ON EFFICIENCY OF CORROSION

Inasmuch as the efficiency of corrosion is found to vary greatly under different conditions, it was deemed advisable to investigate whether the depth to which a pipe is buried below the surface would have any effect on the efficiency of corrosion. Accordingly a number of specimens were prepared and buried in earth to distances varying from a few inches to about 6 feet. A check specimen was provided in each case to permit correction for self-corrosion, and it was so shielded as to prevent the passage of any current through it. The anodes and check specimens alternated with each other in the order given in Table 4. In correcting for self-corrosion the mean of the losses on the check specimens on both sides of each anode was used. The specimens were buried in virgin red clay soil and were run at an average current density

of about 0.056 milliamperes per square centimeter for about 1490 hours. The results of the tests are shown in Table 4 and plotted

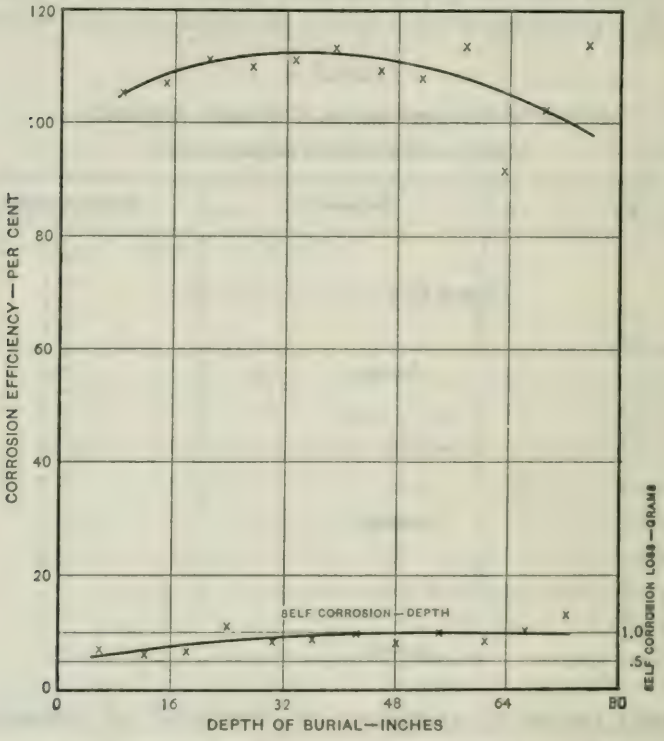

Fig. 7.—*Effect of Depth of Burial on Efficiency of Corrosion*

in Fig. 7, which gives curves of both self-corrosion and efficiency of corrosion as a function of depth.

TABLE 4

Effect of Depth of Burial on Natural and Electrolytic Corrosion

[Wrought-iron cylinders 5.1 cm long and 4.4 cm in diameter polished. Odd numbers carried current; even numbers are for natural corrosion. Area of surface, 70.9 square centimeters. Mean current density, about 0.056 milliamperes per square centimeter]

No.	Total loss	Electrical loss	Theoretical loss	Per cent efficiency of corrosion	Depth
	g	g	g		Inches
1	9.260	7.972	6.990	114	75
2	1.288				72
3	9.475	8.319	8.119	102	69
4	1.024				66
5	7.630	5.685	6.280	91	63
6	.875				60
7	10.862	9.929	8.785	113	57
8	.991				54
9	9.422	8.512	7.890	108	51
10	.829				48
11	8.505	7.593	6.959	109	45
12	.995				42
13	8.822	7.866	6.942	113	39
14	.916				36
15	8.225	7.341	6.618	111	33
16	.852				30
17	6.899	5.913	5.385	110	27
18	1.120				24
19	7.331	6.424	5.780	111	21
20	.694				18
21	4.667	3.993	3.732	107	15
22	.654				12
23	5.092	4.420	4.226	105	9
24	.690				6

It will be seen that the results, while somewhat irregular, indicate that there is but slight variation attributable to depth, although there seems to be a trend upward in the case of self-corrosion. The variation in efficiency of corrosion with depth is probably due to the fact that the moisture content varied with depth. The fact that no greater variation was observed is doubtless due to the fact that the tests were carried out at a time when the soil was fairly wet both near the surface and at greater depths. The results given above on the effect of moisture content indicate that if the experiments had been made in a fairly dry time, when there was

considerable variation of moisture content with depth, the corrosion efficiency would probably have shown a corresponding variation. When conditions are such that there are considerable variations in moisture content with depth, as in a moderately dry time, for instance, the preceding data indicate that the efficiency of corrosion would probably also vary greatly with depth, being in general greater the greater the depth.

5. EFFECTS OF OXYGEN ON CORROSION OF IRON

Since, according to the electrolytic theory of corrosion, the presence of oxygen is an important factor in the production of self-corrosion of iron in the presence of water, it might be expected that the electrolytic corrosion of iron by stray currents would be affected in a marked degree by the content of dissolved oxygen in soil water. In order to investigate this point 10 anodes and a corresponding number of check specimens having an exposed area of 90 square centimeters each were prepared in the usual way, connected in series, and run on a practically constant current density of 0.056 milliampere per square centimeter. Five of these jars were so arranged that oxygen bubbled through the liquid continuously throughout the entire experiment, and the other five were immersed in the water without oxygen being passed through them. At the end of 183 hours the experiment was completed, the anodes were weighed, and the efficiencies of corrosion calculated. The data are given in Table 5, from which it will be seen that there is considerable variation in the efficiencies of corrosion for the individual specimens. These variations are so large that the difference between the average of the five specimens in the jars through which oxygen was passed (98.5 per cent) and the average for those specimens in the remaining jars (91 per cent) has but little significance. It is of course necessary to bear in mind in interpreting these results that even the water through which oxygen was not passed contained a good deal of oxygen in solution, so that any differences in efficiency of corrosion that might be indicated would be those due to a somewhat indefinite difference in the oxygen contained in the water.

TABLE 5

Effect of Oxygen on Efficiency of Corrosion

[Current density, 0.056 milliampere/cm²; time, 183 hours; area of anodes, 90 cm²]

A. OXYGEN ADDED

No.	Total loss	Self-corrosion	Electrical loss	Efficiency of corrosion
	g	g	g	Per cent
0	1.248	0.182	1.066	110.7
1	1.251	.312	.939	97.5
2	1.296	.330	.966	100.5
[5]3	.993	.067	.929	96.5
4	1.128	.327	.801	87.0
	Average			98.5

B. NO OXYGEN ADDED

[5]5	0.886	0.030	0.873	90.6
6	.940	.027	.913	94.9
7	.913	.029	.884	91.7
8	.889	.030	.859	89.0
9	.895	.040	.855	88.7
	Average			91.0

[5] Buried in sand.

TABLE 5a

Effect of Oxygen on Efficiency of Corrosion

[Theoretical loss, 0.730 gram; area of anodes, 15.2 square centimeters; current density, 1.45 milliamperes/cm²]

WITHOUT OXYGEN

No.	Solution	Weights in grams		Loss	Corrosion efficiency
		Original	Final		
		g	g	g	Per cent
1	H_2O	51.326	50.624	0.702	96.2
2	H_2O	51.570	50.871	.699	95.8
3	10% Na_2SO_4	52.361	51.651	.710	97.3
4	10% Na_2SO_4	51.642	50.935	.707	96.9
	Average				96.5

TABLE 5a—Continued

WITH OXYGEN

No.	Solution	Weights in grams		Loss	Corrosion efficiency
		Original	Final		
		g	g	g	Per cent
5	H_2O	51.852	51.154	0.698	95.7
6	H_2O	52.725	52.044	.681	94.7
7	10% Na_2SO_4	51.467	50.759	.708	97.0
8	10% Na_2SO_4	51.034	50.317	.717	98.2
	Average				96.4

In order to check this result more carefully, two series of experiments were carried out, in which a much larger difference in the oxygen content in the two cases was maintained. In each series four specimens were used, two being placed in tap water and the other two in a 10 per cent solution of sodium sulphate. In one series the liquids were first boiled down to about half their original volume in Erlenmeyer flasks to remove oxygen and the iron electrodes inserted during boiling. After the boiling an atmosphere of hydrogen was introduced into the flasks as they cooled down, so that practically no oxygen could have access to the liquid. In the other series air was caused to bubble through the liquid throughout the experiment, so that an abundant supply of oxygen was always present. The results are given in Table Va. From this table it will be seen that there is no appreciable difference between the efficiencies of corrosion in the presence of oxygen and in the absence of oxygen, at least in the liquid electrolytes here used. We have reason to believe, however, that this is not the case when the anodes are buried in soils, although just why a difference should exist here is not clear. That there is a difference is borne out by a number of tests we have made with anodes buried in earth in hermetically sealed cans and others buried in cans exposed to the atmosphere, conditions as to moisture content, current density, etc., remaining the same. Whenever the tests were continued for a considerable time, it was found that the efficiency of corrosion in the sealed receptacle was in nearly all cases considerably lower than when the container remained open. This effect is shown in Table 6.

TABLE 6

Corrosion Efficiencies in Open and Closed Cans

[Average current density, 0.494 milliampere per cm²; area of anodes, 9.4 cm²]

No.	Efficiency of corrosion		No.	Efficiency of corrosion	
	Closed cans	Open cans		Closed cans	Open cans
1	87.9	.....	8	.....	106.5
2	77.4	.....	9	.....	105.5
3	95.2	.....	10	.....	105.3
4	79.9	.....	11	.....	105.5
5	95.4	.....			
6	77.2	.....	Average.....	85.5	105.7
7	85.8	.....			

The average corrosion efficiency in the closed cans was 85.5 per cent, while that in the open cans was 107.5 per cent. Whether or not this difference is due to the difference in the amount of oxygen or CO_2 present or to other causes, it affords another indication of the danger of drawing conclusions from experiments made in liquid electrolytes as to what would occur in the case of electrodes buried in soils.

6. EFFECT OF OXYGEN ON THE END PRODUCTS OF CORROSION

One very marked effect of oxygen on corrosion, however, is its influence on the final products of electrolysis. There is a very common impression extant that the final products of corrosion of iron due to stray currents are the black oxids, whereas in the case of self-corrosion red oxids are produced. This is not in accord with accepted theories of corrosive processes, and the following experiments have been carried out in order to demonstrate that in general this is not the case, although under certain circumstances the tendency may be in that direction.

Four tests were made in which ingot iron was allowed to corrode naturally in the absence of oxygen, one test being in distilled water, two in tap water, and one in 10 per cent Na_2SO_4 solution. Four tests were made in which the iron was allowed to corrode naturally in the presence of oxygen, two tests being in distilled water and two in tap water. Four tests were made in which the iron was allowed to corrode electrolytically in the absence of

oxygen, the electrolyte being tap water in two of the tests and 10 per cent Na_2SO_4 solution in the other two. Four tests were also made in which the iron was allowed to corrode electrolytically in the presence of oxygen, two tests being in tap water and two tests in 10 per cent Na_2SO_4 solution.

The solutions were prepared practically free from oxygen by boiling down to about half their original volume in Erlenmeyer flasks. The iron test pieces were introduced during the boiling, and after the boiling was stopped the flasks were closed off from the air and a current of hydrogen free from oxygen was allowed to pass into the flasks as they cooled down, thus keeping the solutions under an atmosphere of hydrogen.

In the case of the natural corrosion tests in the absence of oxygen, the iron showed no corrosion at first, but after a day or two a a few spots of greenish-black rust were noted, which gradually became larger as time went on, with the formation of a small amount of yellow ferric oxide. This was probably due to the fact that the air gradually diffused in through the rubber connections. In the case of the natural corrosion tests in the presence of oxygen, the rust was soon apparent and consisted almost entirely of the yellow ferric oxide. Thus we see that when oxygen is almost entirely excluded, the ferrous oxide predominates, and when oxygen is present, the ferric oxide predominates.

In the case of the electrolytic corrosion tests, the eight flasks were connected up in series, and a current of about 0.025 amperes allowed to pass for about 27 hours. At the end of this time the current was stopped and the anodes were taken out and weighed and the loss in weight determined. It was found that the corrosion efficiency was practically 100 per cent in all cases, calculating with iron having a valence of two. In the case of the four flasks from which air was excluded, the iron was practically all in the ferrous condition, the corrosion products having the pale green color of the hydrated ferrous oxide. Analysis of the corrosion products in one of the flasks gave 98.9 per cent ferrous iron, the slight oxidation being probably due to the unavoidable introduction of air into the flask during the removal of the electrodes for weighing. Through two of the other four flasks a current of air was allowed to bubble during the course of the electrolysis, and

in those two flasks the corrosion products had the reddish-yellow color of the hydrated ferric oxide, showing that the iron was largely oxidized to the ferric condition. The other two flasks were left open to the air, but air was not bubbled through, and in these flasks the corrosion products had a darker color and when filtered off, dried, and tested with a magnet showed the presence of considerable magnetic oxide. Evidently then, the corrosion had proceeded so fast that there was not enough oxygen present to oxidize the oxide completely to the ferric condition, but in the other case, where air was bubbled through the solution, the solution was kept saturated with oxygen and so the oxide was converted completely to the ferric condition.

These results show that when iron corrodes electrolytically, it corrodes as the ferrous oxide, and that the formation of higher oxides is due to the oxidation of the ferrous oxide by the oxygen of the air, the degree of oxidation depending on the rate of corrosion and the concentration of the oxygen. If the rate of corrosion is relatively rapid and the concentration of the oxygen is relatively low, there will be predominance of the lower oxides, i. e., the ferrous oxide and the magnetic oxide. On the other hand, if the reverse is the case, i. e., if the rate of corrosion is relatively low, there will be a predominance of the ferric oxide.

The same explanation will apply to natural corrosion. In this case the rate of corrosion is very slow, and so the ferric oxide predominates; and even when the oxygen is almost entirely excluded, the rate of corrosion is so slow that there is a slight formation of ferric oxide, although the ferrous oxide predominates.

From the foregoing it will appear that the character of the end products of corrosion does not depend essentially on the cause of the corrosion, but that either of the oxides may be produced, both in the case of self-corrosion and in the case of electrolytic corrosion. It may, however, throw some light on the question in many circumstances, for the reason that the rate of natural corrosion of pipes embedded in earth may usually be expected to be so low that practically nothing but the ferric oxides would be produced, there being enough oxygen in the soil waters to oxidize any ferrous iron that may be formed. In the case of electrolytic corrosion, however, this will not always be the case, the corrosion being so

rapid, especially under bad electrolysis conditions that the supply of oxygen in the ground waters will not be sufficient to oxidize all of the ferrous iron, and the result will be the formation of a considerable amount of magnetic oxide. This, however, will no doubt be largely affected by the depths of the pipe below the surface. The deeper the pipes, as a rule, the less would be the available supply of oxygen, and the greater would be the tendency for the formation of the magnetic oxide. Pipes very close to the surface even though corroding very rapidly by stray currents, might still form little, if any, magnetic oxide, because of the abundant supply of oxygen that would be available. Nevertheless, wherever a large preponderance of magnetic oxide exists, while it does not definitely prove that the corrosion has been due to stray currents, it may usually be regarded as a good indication that the rate of corrosion has been so great as to make it altogether probable that stray currents have been largely responsible, unless soil conditions, such as the presence of cinders, coke, chemicals, etc., are such that extremely rapid self-corrosion may be indicated.

7. RELATIVE ELECTROLYSIS IN DIFFERENT KINDS OF IRON

The question as to relative tendencies of different kinds of pipe to suffer damage due to electrolysis has often been discussed, and there appears to be a well-defined feeling in many quarters that a marked difference of this sort exists. It seems to be the general impression that cast-iron pipes are much less susceptible to electrolytic damage than wrought-iron or steel pipes. Experience indicates that cast-iron pipe does show less trouble from electrolysis than other kinds under most conditions. It has often been contended that certain kinds of iron are more resistant to self-corrosion than others, cast iron suffering less than either wrought iron or steel. Since the experimental data presented later in this paper show that the natural corrosion is affected in a marked degree by the presence of stray currents, it might reasonably be supposed that different kinds of pipes would also suffer in widely varying degrees from stray-current corrosion. In order to determine to what extent this might be the case, a considerable number of experiments have been carried out, using different kinds of iron that are employed in commercial service for under-

ground pipes. Four kinds of iron were used, namely, ingot iron, which is the purest commercial iron known, wrought iron, machine steel, and cast iron. Two series of experiments were run on cast iron, in one of which the cast iron was machined to a clean surface and in the other the iron was used just as it came from the mold, without removal of the scale. The test specimens, weighing about 30 grams each, were placed in a red-clay soil practically saturated with water and run in series on a constant current, so that the same number of ampere hours was discharged from each test specimen. The results are shown in Table 7. Since the current in all specimens was the same, and the size of the test specimens practically the same, giving about 0.2 milliampere per square centimeter, the figures shown in the column under "electrical loss" are directly comparable for the different kinds of iron and show the relative tendency of the iron to corrode electrolytically under conditions of the test.

TABLE 7

Comparative Corrosion Efficiency for Ingot, Wrought, and Cast Iron, and Machine Steel

1. INGOT IRON

No.	Total loss	Self-corrosion	Electrical loss
	g	g	g
0	1.704	0.015	1.689
3	1.678	.033	1.645
4	1.848	.051	1.797
5	1.669	.031	1.638
6	1.791	.043	1.748
7	2.243	.046	2.197
8	1.665	.041	1.624
9	1.583	.074	1.509
10	1.688	.036	1.652
11	1.713	.060	1.653
12	1.706	.033	1.673
13	1.676	.042	1.634
14	2.167	.055	2.012
15	1.661	.028	1.633
16	1.679	.076	1.603
17	1.674	.046	1.628
18	1.648	.058	1.590
19	1.647	.057	1.590
Average		.046	1.695

TABLE 7—Continued

2. MACHINE STEEL

No.	Total loss	Self-corrosion	Electrical loss
	g	g	g
20	1.658	0.052	1.606
23	1.734	.076	1.650
24	1.827	.062	1.765
25	1.721	.066	1.655
26	1.672	.064	1.608
27	1.694	.076	1.618
28	1.684	.113	1.571
29	1.756	.087	1.669
30	1.644	.031	1.613
31	1.653	.046	1.607
32	1.792	.066	1.726
33	1.761	.059	1.502
34	1.686	.033	1.653
35	1.695	.063	1.632
36	1.808	.066	1.742
37	1.734	.066	1.668
38	1.818	.109	1.709
39	1.694	.059	1.635
Average		.066	1.652

3. WROUGHT IRON

40	1.713	0.160	1.533
43	2.203	.077	2.126
44	1.789	.065	1.724
45	1.712	.063	1.649
46	1.689	.117	1.572
47	1.842	.094	1.748
48	1.756	.116	1.640
49	1.693	.069	1.624
50	1.659	.048	1.611
51	1.201	.114	1.087
52	1.701	.124	1.577
53	1.661	.068	1.593
54	1.852	.055	1.797
55	1.684	.068	1.616
56	1.646	.050	1.596
57	1.712	.073	1.639
58	1.713	.076	1.637
59	1.840	.080	1.760
Average		.084	1.696

TABLE 7—Continued

4. CAST IRON SURFACED

No.	Total loss	Self-corrosion	Electrical loss
	g	g	g
60	1.807	0.120	1.687
63	1.700	.305	1.395
64	1.846	.108	1.738
65	1.757	.283	1.474
66	1.769	.177	1.592
67	1.746	.079	1.667
68	1.808	.136	1.672
69	1.939	.082	1.857
Average		.161	1.635

5. CAST IRON UNSURFACED

70	1.712	0.136	1.576
71	1.435	.255	1.180
74	1.810	.047	1.763
75	1.709	.060	1.649
76	1.868	.245	1.623
77	1.710	.135	1.575
78	1.662	.252	1.410
79	1.712	.060	1.652
Average		.149	1.553

An examination of these figures shows that there is but little difference in the amount of corrosion in the different kinds of iron. This is particularly true of the wrought iron, machine steel, and machined cast iron, which show, respectively, 1.641, 1.656, 1.635 grams loss. The ingot iron showed a somewhat higher electrolytic corrosion than any of the others, which seems to be somewhat surprising in view of the fact that it has frequently been found that the self-corrosion in the case of ingot iron is less than others. The least corrosion of all was in the case of the unfinished cast iron, and this is probably due to the protective effect of the scale, but even here the difference is hardly great enough to be considered of practical importance. The conclusion that must be drawn from these figures is that the efficiency of electrolytic corrosion of the different kinds of iron pipes is practically the same. If we examine the columns show-

ing the self-corrosion in different kinds of iron we find very surprising differences. These check specimens were placed in the can along with the anodes and carefully shielded from the flow of current as in all previous cases. An examination of these data shows that ingot iron gave the least corrosion of all, the average for all the specimens being 0.046 grams. Machine steel came next with a total natural loss of 0.066 grams; wrought iron is third with 0.084 grams; and last, and most surprising of all, the self-corrosion of the cast iron is very much higher, being 0.161 for the machined iron and 0.149 for the unfinished iron. This shows but little difference between the finished and unfinished cast iron in the matter of self-corrosion in the presence of current flow. The relatively high rate of self-corrosion of cast iron as compared to the other kinds of iron tested is contrary to the generally accepted idea that cast iron is more resistant to self-corrosion than wrought iron. It is not improbable that this impression in regard to the superiority of cast iron has grown out of the fact that cast iron structures are usually made relatively heavy and they also tend to corrode more uniformly than wrought iron or steel, both of which factors would tend greatly to increase the life of the former. The principal cause of the greater rate of self-corrosion of cast iron appears to be the galvanic action set up between the free carbon and the iron. The carbon is distributed so uniformly throughout the mass, however, that no appreciable pitting results, and hence the corrosion is less conspicuous and also less important than the same amount of corrosion would be if not uniformly distributed as is usually the case of most other kinds of commercial iron. It should be pointed out here that these tests were carried out in the same kind of soil as that used in securing the data of Table 1, and the partial analysis there given shows it to be low in chlorides, sulphates, carbonates, and nitrates. It was also free from cinders, coke, etc., and hence is not to be regarded as a very corrosive soil. It is shown later in this paper that the chemical constituents in the soil have a marked influence not only on the total corrosion but also on the pitting, or uniformity of the corrosion, so that it should not be assumed that the relative values given here will hold for all soils.

The foregoing results show that the different kinds of iron do not in themselves differ materially as regards their tendency to corrode electrolytically. It would appear from this that the differences noted in practice, particularly in favor of cast iron, are due to various other causes, as has already been pointed out by Prof. Ganz and others, namely, higher resistance joints, higher specific resistance of the iron, the heavier walls, and a tendency to corrode more uniformly.

8. EFFECT OF CERTAIN CHEMICALS ON THE CORROSION OF WROUGHT IRON IN EARTH

When pipes are buried in the streets, they are subject not only to the action of the moisture and various natural constituents of the soil, but also to the effects of such chemicals as may result from the traffic on the streets, or from other sources.

A large amount of work has been done by other investigators on strips of iron immersed in aqueous solutions, and it has been shown that the resulting corrosion is a function of the amount as well as the character of the chemical used. In many cases the tendency toward self-corrosion first increases with the concentration and later diminishes very rapidly, possibly to zero, when the concentration is sufficiently increased.

It is well known also that certain solutions, such as alkalies, chromates, etc., tend strongly to inhibit electrolytic corrosion, at least when such solutions are practically pure. Hayden has shown that solutions of chromates, for example, tend to produce passivity in iron and thus prevent electrolytic corrosion, but that this passivity is destroyed by the addition of a few hundredths of 1 per cent of a chloride or a somewhat greater quantity of sulphate. It was considered advisable to carry out a series of experiments with iron embedded in earth to which various chemicals had been added.

For these experiments a number of acids, bases, and salts as indicated in Table 8 were secured and 2 grams of each were added to 300 g of distilled water. The solution was added to 700 g of air dried red clay, which had been sifted through a 20-mesh sieve. This earth contained initially about 5 per cent of moisture, so that the resulting mixture contained about 33 per cent water, which

produced a fairly wet earth. The whole was thoroughly mixed and placed in a quart tin fruit can provided with friction top.

The anodes were prepared as in experiments already described and vessels of water were placed in the cans as in previous experiments and the cans connected in series; first, in one group; finally, on account of increased resistance, in three. The current was adjusted daily to 0.005 ampere, which gave a current density of discharge of about 0.45 milliampere per square centimeter.

At the end of 85 days the experiment was discontinued, the cylinders cleaned as previously described, and the losses computed.

In Table 8 the substances have been grouped according to the anions formed. Since in a number of cases more salt was used than the water could dissolve, the solubility of each chemical has been indicated. This is followed by the number of grams of the anhydrous salt used per liter of water. Then follows the chemical value of the solution, i. e., the number of grams of salt per liter of water multiplied by the hydrogen value of the anion and divided by the molecular weight of the salt.

TABLE 8

Effect of Chemicals on Corrosion

1	2	3	4	5	6	7	8	9	10
Chemical	Can No.	Solubility (g per liter)	Solution (g per liter)	Chemical value	Critical value (g per liter)	Limiting value (g per liter)	Efficiency of corrosion at (0.55 m. a. per sq. cm.)	Self-corrosion loss (Mg per sq. cm. per day) BS	Corrosion efficiency obtained by Hayden 1 per cent sol. (0.22 m. a. sq. cm.)
CH_3COOH	2	.....	5.715	0.0957	.....	.....	102.5	0.109	.....
$KMnO_4$	28	63.4	5.715	.0364	0.1	0.1–1.0	90.2	.166	.....
$Ba(NO_3)_2$	34	92.	5.175	.0441	.....	.....	123.2	.150	.....
$(NH_4)NO_3$	10	1924.	5.715	.0719	0–500	1155	116.3	.265	37.8
$NaNO_3$	16	880.	5.715	.0677	.1	632	104.2	.152	.....
KNO_3	22	316.	5.715	.0571	.....	.....	89.6	.238	25.
HNO_3	4	.....	5.715	.0914	.....	.....	85.4	.506	.....
Average	.....	.....	.....	.....	.....	.....	103.7	.262	.....

TABLE 8—Continued

1	2	3	4	5	6	7	9	9	10
Chemical	Can No.	Solubility (g per liter)	Solution (g per liter)	Chemical value	Critical value (g per liter)	Limiting value (g per liter)	Efficiency of corrosion at (0.55 m. a. per sq. cm.)	Self-corrosion loss (Mg per sq. cm. per day) BS	Corrosion efficiency obtained by Hayden 1 per cent sol. (0.22 m. a.) sq. cm.)
$BaCl_2$ (2 H_2O)	31	357.	4.874	.0479	0	374	106.0	.136	.....
$CaCl_2$ (2 H_2O)	25	427.	2.890	.0526	.....	.....	101.8	.159	.....
HCl	1	.....	5.715	.1579	.....	.....	101.6	.270	.....
NH_4Cl	7	372.	5.715	.1076	1.0	290	101.4	.496	102.3
KCl	19	340.	5.715	.0772	50.0	299	98.6	.222	102.2
NaCl	13	3582.	5.715	.0985	0	395	97.8	.239	.....
Average	.....	.....	.....	.....	.....	.....	101.2	.253	.....
Na_2SO_4 (10 H_2O)	18	194.	2.520	.0260	10.0	400	89.2	.136	.....
K_2SO_4	24	111.	5.715	.0661	0	108	88.9	.170	102.8
$BaSO_4$	36	0.002	5.175	.0494	.....	.....	87.7	.231	.....
H_2SO_4	5	.....	5.715	.1174	.....	.....	87.4	.329	.....
$(NH_4)_2SO_4$	12	754.	5.715	.0873	0–200	534	86.0	.316	102.7
$CaSO_4$ (2 H_2O)	30	2.	4.520	.0669	0	.....	85.9	.174	.....
Average	.....	.....	.....	.....	.....	.....	87.5	.226	.....
Ba $(OH)_2$ (8 H_2O)	32	39.	3.104	.0365	0	3.1	93.1	.322	.....
NH_4OH	8	526.	11.770	.6965	.....	.....	88.7	.591	.....
KOH (2 H_2O)	20	1120.	3.480	.0348	.....	.....	85.6	.611	.....
NaOH (1 H_2O)	14	1090.	3.942	.0993	.1	1.0	81.7	.608	.....
HOH (Av)	3 & 33	.....	.....	.....	.....	.....	73.9	.268	.....
Ca $(OH)_2$	26	1.6	5.715	.1556	0	.67–1.35	73.5	.195	.....
Average	.....	.....	.....	.....	.....	.....	82.7	.431	.....
K_2CO_3	21	1120.	5.715	.0834	1.0	1–10	89.3	.306	2.75
Na_2CO_3 (1 OH_2O)	15	275.	2.107	.0201	1.0	10	85.4	.394	.....
$(NH_4)_2CO_3$	9	1000.	5.715	.1225	.....	.....	81.7	.561	38.2
$CaCO_3$	27	0.01	5.715	.0719	.0003	.28	66.2	.348	.....
Average	.....	.....	.....	.....	.....	.....	80.6	.402	.....
$BaCrO_4$	35	0.004	5.715	.0455	.....	.....	45.0	.189	.....
$(NH_4)_2CrO_4$	11	405.	5.715	.0762	.....	.....	0.4	.003	.....
$CaCrO_4$ (2 H_2O)	29	142.	4.643	.0640	.....	.....	0.3	.136	.....
K_2CrO_4	23	632.	5.715	.0593	0	.1 up	0.3	.163	.....
Na_2CrO_4 (10 H_2O)	17	813.	2.829	.0354	.....	.....	0.3	.082	.....
CrO_3	5	657.5	5.715	.1143	0	.01–.05	−0.2	.122	.....
Average	.....	.....	.....	.....	.....	.....	.....	.116	.....

Then follow two columns of values obtained from Hein and Bauer's "On the attack of iron in water and aqueous solutions." [5] The first is the concentration of solution giving maximum corrosion; the second the concentration producing passivity or minimum corrosion. Hein and Bauer suspended small iron plates in beakers of solutions of concentrations from zero to saturation. Their researches in this line are more extensive than any other work so far reported.

While their experiments can not be compared with the one now recorded on account of differences in conditions, the values quoted may indicate at what part of the corrosion-concentration curve the present tests were made, from which we may form some estimate as to the manner in which the corrosion would have changed if the concentration were varied. The efficiency of corrosion is given in the following column, and this is followed by the natural loss in milligrams per square centimeter of surface of the iron per day.

Referring to the efficiencies of corrosion given in column 8, it will be seen that with the exception of chromate compounds the efficiencies of corrosion are comparatively high.

All of the soluble chromates seem to protect the iron from electrolytic corrosion, though this protection is not quite complete. In the case of chromium trioxide the loss at the anode was slightly less than that of the check specimen. No significance should be attached to this result until after further investigation. The comparatively slight protection shown by barium chromate is no doubt due to its very slight solubility.

None of the other chemicals which Friend, Hein and Bauer, or Hayden have found to render iron passive in solutions seem to have been effective. Indeed, excepting the chromates there are but two values less than the average corrosion efficiency when distilled water was used.

The anodes in cans containing chromates were blackened, and making the iron cathode in 2 per cent H_2SO_4 for half an hour did not remove the discoloration. The check specimens were not discolored in this way.

[5] Mittellungen aus dem Königlichen Material-prüfungsamt. 1908 Berlin 26, 1

That the hydroxids did not protect the iron may have been due to the presence of materials in the soils which neutralized them. There was no doubt considerable CO_2 in the soil since it had been dried, crushed, and sifted in the laboratory and had stood there in an open barrel for some time, and this may have been sufficient to counteract the effect of the hydroxids.

As will be seen by comparing columns 4 and 7 the concentrations used in the case of the hydroxids and carbonates were in nearly every case greater than those producing passivity when the solution alone acts on the iron. The difference in the results may be due to the effect of the earth on the solution or to the effect of the current. It seems clear, however, that the conditions which prevent self-corrosion are not in general those which will maintain passivity in the case of anodes discharging current at moderate current densities. There does not appear to be any very definite relation between the corrosion efficiency observed and the self-corrosion. The nitrates and chlorides for instance show respectively 103 and 101 per cent efficiencies of corrosion with corresponding value of self-corrosion of 0.262 and 0.263 mg per square centimeter per day. The hydroxids and carbonates show lower corrosion efficiencies, namely, 82 and 80 per cent, respectively, but the self-corrosion is much higher, being 0.431 for the hydroxid and 0.402 for the carbonate. The soluble chromates show almost a complete absence of electrolytic corrosion, whereas the self-corrosion, although smaller than in the other cases, is by no means so small in proportion. It will be seen, also, that the corrosion efficiencies observed do not agree with the values found by Hayden,[6] and shown in column 10. While a part of this difference may be due to the differences in solution strength and current density, it is probably due for the most part to the fact that the tests in the present instance were carried out with anodes embedded in earth, whereas the experiments of Hayden were carried out in water solutions.

It does not seem probable that a sufficient quantity of inhibiting chemicals can be added to the soil surrounding a buried pipe to protect it indefinitely at a reasonable cost. To render the pipe

[6] Jour. of the Franklin Institute, v. 172, p. 295.

passive is one problem; to maintain it passive against fluctuating, or even reversing currents regardless of the action of the soil and the constantly changing soil waters on the soluble chemical, is quite another.

A phenomena of importance which is not shown in the tabulated data, is the pitting of the iron. This is usually attributed to particles of impurities in the surface of the iron or to variations in the soil. In these experiments the virgin soil was dried, rolled, and sifted through a 20-mesh sieve. Enough solution was added to nearly saturate the soil. All of the cylinders were cut from the same piece of Norway iron rod. It might be expected, therefore, that the pitting would be very similar in all cases. This, however, was by no means the case. The anodes from the nitrate cans were covered by a dark cheese-like layer which maintained the original form of the anode. When this was pared off the surface of the iron was nearly smooth, showing the fibrous structure of the wrought iron but no pits. The anodes in the cans containing sulphates were corroded almost as uniformly; the surface of the cleaned anodes was brighter and somewhat uneven but showed no marked pits. The surface of the anodes from the carbonate cans was more uneven. Pitting is noticeable in the case of the hydroxids and very marked in anodes from the cans containing chlorids.

As has been stated the soluble chromates blackened the surfaces of the anodes but did not materially attack them otherwise. There are no marked differences in the appearance of the check specimens except that those from the chromate cans remained bright. So marked are the differences in the anodes that in most cases it is possible to classify them by their appearance without reference to their numbers.

As underground pipes are almost always destroyed by pitting rather than by the amount of iron lost, a satisfactory means of preventing pitting would be of great value. The remedy most commonly suggested is the use of a more homogeneous iron. Without doubt this would reduce the corrosion due to local galvanic action, but the above experiments indicate that pitting of buried iron is very largely influenced by the nature of the electrolyte in the soil.

It may seem that for comparing the effects of different chemicals quantities which are chemically equivalent should be chosen. A glance at columns 5 and 8 will show that in a number of cases practically equal corrosion efficiencies occur when the chemical values are very different. Indeed, so far as the tables go, there seems to be no relation between chemical values and corrosion efficiency.

It appears from these experiments that solutions which produce passivity when iron is immersed in them do not protect the iron against electrolytic corrosion when the solutions are in earth, and with the exception of the chromates, no chemicals here tried are of marked value in reducing corrosion. Also, the action of iron in a solution is not a safe criterion of its behavior when the iron is made anode in earth containing these solutions.

9. CORROSION IN SOILS FROM DIFFERENT SOURCES

While the foregoing experiments show the effect of the different factors which influence electrolytic corrosion in soils, it naturally raises the question as to what extent these various factors are acting in the case of iron pipes subjected to electrolysis under practical conditions. This question seems to be best answered by actually carrying out experiments on electrolytic corrosion in a great variety of soils of different kinds and gathered from widely different sources, at the same time maintaining the conditions as near to practical conditions as possible. In order to do this, corrosion tests were made on a large number of samples of soils which were gathered from various cities and sent to the Bureau of Standards at Washington for test as to their various physical properties. Ninety-seven such samples were used for these corrosion tests which were taken from various places in Philadelphia, Pittsburgh, Erie, and Apollo, Pa.; St. Louis, Mo.; Butte, Mont.; and Albuquerque, N. Mex. Practically all of these soil samples were taken from excavations made for the purpose of examining pipes and were taken at about the same depth as the pipe in most instances. In all cases the samples were put at once into hermetically sealed cans and kept therein until ready for test. For the purpose of making the corrosion tests the soils were divided into two classes. Those soils from Philadelphia, St. Louis, Butte,

and Albuquerque were saturated with distilled water and kept so throughout the tests. The current density of the discharge averaged about 0.0002 ampere per square centimeter. The soils from Pittsburgh, Erie, and Apollo, Pa., were tested with the same moisture content which they had when taken from the ground, and the current density was maintained at about 0.001 ampere per square centimeter. We thus have for one set a very wet soil and a rather low current density, and in the other a rather high current density with what may be considered as roughly average moisture content, since at the time the samples were taken the soil was neither unusually wet nor unusually dry. The results of these efficiency of corrosion tests are given in Table 9. An examination of specimens 1 to 85, in which the earth was very wet and the current density low, shows quite high efficiencies of corrosion, the extreme ranges being 87.9 per cent for specimen No. 2 and 126.3 per cent for No. 30. All but four show values exceeding 100 per cent, while the great majority fall between 100 per cent and 115 per cent, the average of all being about 107 per cent.

TABLE 9

Corrosion Efficiency Tests on Soils from Different Sources

Rod No.[a]	Total loss	Self-corrosion	Electrical loss	Theoretical loss	Corrosion efficiency
	g	g	g	g	Per cent
1	2.294	0.114	2.180	1.867	116.8
2	1.811	.170	1.641	.....	87.9
3	2.147	.062	2.085	.....	111.9
4	2.244	.195	2.049	.....	110.0
5	2.327	.090	2.237	.....	119.8
6	2.203	.117	2.086	.....	112.1
7	2.156	.075	2.081	.....	111.9
8	2.244	.175	2.069	.....	111.0
9	2.273	.089	2.084	.....	116.7
10	2.363	133	2.230	.....	118.8
11	1.881	064	1.817	.....	97.3
12	2.103	.174	1.929	.....	103.4

[a] Nos. 1 to 37, inclusive, taken from Philadelphia, Pa.; Nos. 38 to 47, inclusive, taken from Norristown, Pa.; Nos. 48 and 49 from Albuquerque, N. Mex.; Nos. 50 to 84 from St. Louis, Mo.

TABLE 9—Continued

Rod No.	Total loss	Self-corrosion	Electrical loss	Theoretical loss	Corrosion efficiency
	g	g	g	g	Per cent
13	2.173	.126	2.047	1.876	109.2
14	1.992	.025	1.967	.....	104.8
15	2.052	.308	1.744	.....	.....
16	2.584	.280	2.304	.....	122.8
17	2.186	.041	2.145	.....	114.4
18	2.207	.032	2.175	.....	115.9
19	2.052	.086	1.966	.....	104.8
20	1.804	.103	1.701	.....	.....
21	2.058	.091	1.967	.....	104.8
22	2.187	.130	2.057	1.871	109.9
23	2.168	.203	1.965	.....	105.0
24	2.091	.044	2.047	.....	109.4
25	2.220	.045	2.175	.....	.....
26	2.239	.078	2.261	.....	120.9
27	2.398	.112	2.286	.....	122.3
29	2.091	.068	2.023	1.895	107.0
30	2.497	.108	2.389	.....	126.3
32	2.190	.044	2.146	.....	103.6
33	2.130	.079	2.051	.....	108.4
34	2.068	.061	2.007	.....	106.0
37	2.310	.170	2.140	.....	113.2
38	2.114	.097	2.017	.....	106.4
39	2.362	.085	2.277	.....	102.4
40	2.375	.193	2.182	.....	115.6
41	2.300	.025	2.275	.....	120.2
42	2.313	.155	2.158	.....	113.7
43	2.161	.150	2.011	1.913	105.0
44	2.148	.094	2.054	.....	107.3
45	2.202	.031	2.171	.....	113.4
46	2.105	.182	1.923	.....	100.7
47	2.257	.101	2.156	.....	112.8
48	2.489	.351	2.138	.....	111.7
49	2.126	.022	2.104	.....	110.2
50	2.177	.121	2.056	.....	107.3
51	2.188	.122	2.066	.....	107.9
52	2.305	.104	2.201	.....	116.1
53	2.200	.148	2.052	.....	107.3
54	2.250	.228	2.022	.....	105.7
55	2.108	.052	2.056	.....	107.4
56	2.330	.117	2.213	.....	115.6
57	2.252	.115	2.137	.....	111.7
58	2.206	.156	2.050	.....	107.2
59	2.258	.247	2.011	.....	105.2
60	2.194	.133	2.061	.....	107.8
62	1.318	.054	1.264	.....	66.2
63	2.201	.143	2.058	.....	107.6

TABLE 9—Continued

Rod No.	Total loss	Self-corrosion	Electrical loss	Theoretical loss	Corrosion efficiency
	g	g	g	g	Per cent
64	2.242	.068	2.174	1.866	117.2
65	2.224	.157	2.067	.....	116.3
66	2.295	.060	2.235	.....	121.0
67	2.085	.045	2.040	.....	109.9
68	2.164	.060	2.104	.....	113.4
69	2.276	.181	2.095	.....	112.9
71	2.225	.096	2.129	.....	114.7
72	2.210	.156	2.054	.....	110.8
73	2.152	.020	2.132	.....	104.9
74	2.070	.096	1.974	.....	106.4
75	2.190	.100	2.090	.....	112.6
76	2.062	.038	2.024	.....	109.2
77	2.200	.072	2.128	.....	114.6
78	2.089	.151	1.938	.....	104.4
79	2.063	.114	1.949	.....	105.1
81	2.286	.064	2.222	.....	119.8
82	2.152	.157	1.995	.....	107.5
83	2.330	.135	2.195	.....	108.3
84	1.706	.188	1.518	.....	81.8
85	2.062	.003	2.059	.....	111.0

PITTSBURGH, PA., SOILS

Total loss	Self-corrosion	Electrical loss	Theoretical loss	Corrosion efficiency
g	g	g	g	Per cent
4.600	0.207	4.393	4.969	88.4
5.100	.177	4.923	.....	99.2
3.953	.295	3.658	.....	74.7
2.780	.220	2.560	.....	51.6
5.210	.030	5.180	.....	104.3
4.368	.005	4.363	.....	87.8
5.195	.140	5.055	.....	101.6
2.822	.270	2.552	.....	51.4
3.005	.140	2.865	.....	57.7
4.435	.145	4.290	.....	86.4
3.519	.546	2.973	.....	67.2
4.272	.545	3.727	.....	72.0

ERIE, PA., SOIL

4.932	0.185	4.747	4.750	99.9
3.499	.250	3.249	.....	68.2
4.692	.255	4.437	.....	94.0
3.595	.129	3.466	.....	72.9
4.777	.245	4.532	.....	74.4
18.180	1.451	17.729	.....	80.7
7.531	.040	7.491	.....	36.3

Current density, 1 milliampere per square centimeter.

The figures in the second group show much lower values, the extreme range being between 36.3 per cent and 104.3 per cent. Most of the values fall between 60 and 100 per cent, with an average for all specimens of about 76 per cent. The difference between the efficiencies of corrosion shown by the two series is evidently due partly to the lower moisture content and higher current density in the latter case. These results are in accord with the data already presented in which the effects of moisture and current density have been studied separately. It should be pointed out here that while the current density in the second series is higher than may be expected under average conditions in practice, it is no higher than would frequently be encountered under moderately severe practical conditions. From these and the preceding tests it will be evident that under average practical conditions we may expect the corrosion efficiency to be of the order of 100 per cent when the earth is very wet and the current density quite low, while as the moisture content is reduced or the current density increased the corrosion efficiency falls off and will usually be found to range between 50 and 100 per cent, while in quite dry soils, such as might at times be encountered in practice, a much lower figure might occur. We are convinced that under average conditions of soil moisture, and with current densities that may be expected in localities where electrolysis conditions may be considered moderately severe, a corrosion efficiency between 50 and 110 per cent will usually prevail. It will be seen also from the foregoing data that the decrease in corrosion efficiency due to increased current density is by no means as rapid as the increase in current, so that within the limits of current density that will usually be encountered in practice the actual amount of corrosion will be found to increase with increase of current.

The question may well be raised as to the reliability of corrosion efficiency experiments carried on in earths in the laboratory, and the extent to which such results may be considered as representing what would take place in the earth under normal conditions. In general, however, it will appear that experiments made in the laboratory are much more satisfactory for studying the laws of corrosion because conditions can then be much more readily con-

trolled, and it is simply necessary to determine whether or not the laws of corrosion are substantially the same in the case of experiments on iron embedded in small samples of soil as they would be if the iron were embedded in the earth out of doors, all other conditions being the same. This would probably not be true if the experiments were continued over a great length of time during which certain soluble constituents of the soil in the laboratory specimens might become exhausted by the corrosive processes, but we have ample reason to believe that experiments thus made and extending over a comparatively short time represent quite closely what may be expected to take place in the case of pipes under actual conditions. Numerous experiments have been made on specimens of iron embedded in the earth out of doors in order to check this conclusion and to guard against any serious error that might be introduced by possible conditions of the soil. Some of the data bearing on this have already been given in the earlier part of this report relating to the effects of depth of burial and of current density on efficiency of corrosion, which show that for similar conditions the results for the outdoor tests do not give results materially different from the laboratory tests. Another series is given in Table 10. In this case a number of specimens of iron were buried in the earth out of doors and caused to carry current for several months, and the efficiency of corrosion was determined. The current density varied considerably during the experiments, due largely to change in resistance of the soil, but on the whole the range of current density averaged about the mean of the values used in the tests on effect of current density given above. The moisture content, of course, varied considerably from time to time.

An examination of Table 10 shows that the efficiencies of corrosion in these outdoor tests ranged between approximately the same limits as those carried on indoors for similar ranges of moisture and current density. These data afford additional evidence that the results of the corrosion efficiency experiments carried on on samples of iron embedded in soils in the laboratory are of substantially the same order of magnitude as they would be if the iron had been buried out of doors.

TABLE 10

Efficiency of Corrosion, Specimens Buried in Ground out of Doors

No.	Total loss	Self-corrosion	Electrical loss	Efficiency of corrosion
	g	g	g	Per cent
1	15.719	0.286	15.433	74.9
3	12.159	.286	11.873	72.8
5	4.425	.282	4.143	61.5
6	5.879	.282	5.597	73.9
7	5.894	.280	5.614	80.0
10	6.374	.280	6.094	96.3
11	2.364	.278	2.086	83.3
12	3.310	.278	3.032	76.8
Average				77.9

10. CAUSES OF VARIATIONS IN EFFICIENCY OF CORROSION

The causes which give rise to corrosion less than the theoretical amount according to Faraday's law have been the subject of much investigation by numerous investigators in connection with studies of passivity in iron. Numerous theories have been evolved, but comparatively little is definitely known in regard to this subject. The subject is too complicated and would lead to too much theoretical detail for discussion here. On the other hand, no attention has been given to the influences that may be responsible for corrosion efficiencies greater than 100 per cent, and in view of the frequency with which these high efficiencies of corrosion occur it seems well to present here very briefly a few comments as to the possible causes that may be responsible for these high values.

It has been seen that the efficiency of corrosion of iron embedded in earth in many cases exceeds 100 per cent, although we have not been able to confirm the results of other investigators previously referred to in this paper who have reported electrolytic corrosion amounting to several times the theoretical value. The highest values which we have found in our experiments have been of the order of 150 per cent, but for the most part the corrosion has not been greater than 20 per cent in excess of the theoretical amount. The very large number of cases, however, both among the tests already described and among those that follow, in which the corrosion efficiency exceeds 100 per cent, even after careful correction

has been made for self-corrosion, indicate quite clearly that the loss of iron due to the discharge of electric current is in many cases appreciably greater than the theoretical amount. This is a matter of great importance and is being given special attention with the view of throwing further light on its causes, but much yet remains to be done before the phenomena can be properly understood.

Several causes suggest themselves as possible factors in producing this high efficiency of corrosion, some of which are discussed below.

(a) **Formation of New Galvanic Couples.**—It is well known that when iron corrodes in the presence of water and oxygen oxids of iron are formed as end products. Under most underground conditions these will be deposited at the surface of the iron in more or less irregular contact with the iron. These oxids are fairly good conductors and are also electronegative against iron, so that when a particle of iron oxid comes in actual contact with the iron, a galvanic element is formed which tends to corrode the adjacent iron. It seems not improbable, therefore, that when a clean piece of iron is subjected to the discharge of electric current the formation of the iron oxid which results from the initial corrosion may set up galvanic couples which did not before exist and thus greatly increase the self-corrosion on the specimen.

The following experiments were carried out to gain an idea of the effect of the initial corrosion products on subsequent electrolytic corrosion and on the self-corrosion of the specimen. In this experiment twelve 2-quart tin cans were coated outside with paraffin, and a layer of heavy paraffined paper placed over the sides. The cans were then nearly filled with red clay which had been air dried two months and sifted through a 20-mesh sieve; 300 g of distilled water was added to 700 g of this sifted earth, and the whole thoroughly mixed before it was packed in the cans. This earth was nearly saturated with water. For anodes and check specimens cylinders of ¼ inch Norway iron 2 inches long were used. The cylinders were carefully cleaned and placed vertically in the cans, the anodes in the center and the check specimens close to the side, and carefully shielded from current flow. A small vessel of water was placed within each can to retard evaporation of the moisture in the earth.

The 12 cans were then connected in series on a 115-volt circuit; the cans serving as cathodes. The current was kept practically constant at 10 milliamperes.

At the end of 429 hours 8 cans were removed from the circuit. Four of these were set aside unopened. From the other four the cylinders were removed, cleaned, weighed, and replaced, and the 4 cans were then replaced in circuit.

At the end of 686 hours more the cans were opened, the cylinders cleaned, weighed, and the losses computed. When the cylinders were washed in warm water, practically all of the rust came off, so that it was necessary to clean them electrolytically for but a few minutes to obtain a bright surface.

The corrosion of the anodes was more uniform than in most previous experiments, but the corroded surface was nevertheless somewhat uneven, the loss being greatest near the centers of the cylinders. There was practically no pitting of the check specimens.

The results of the experiments are shown in the following Table 11:

TABLE 11

Effect of Initial Products on Subsequent Corrosion

[Area of exposed metal, 7.6 cm²; current density, about 1.2 milliamperes per cm²; moisture in soil, about 30 per cent]

GROUP A

No.	Total loss	Self-corrosion	Electrical loss	Efficiency of corrosion
	g	g	g	Per cent
2	4.270	0.085	4.185	102.8
6	4.408	.085	4.323	106.3
7	4.365	.085	4.280	105.2
12	4.370	.085	4.285	105.3
Average				104.8

GROUP B, FIRST PERIOD

1	4.230	0.045	4.185	102.8
3	4.226	.045	4.181	102.7
13	4.225	.045	4.180	102.7
14	4.273	.045	4.228	103.8
Average				103.0

TABLE 11—Continued

GROUP B, SECOND PERIOD

No.	Total loss	Self-corrosion	Electrical loss	Efficiency of corrosion
	g	g	g	Per cent
1	6.316	0.080	6.236	87.8
3	6.645	.080	6.565	92.5
13	6.475	.080	6.395	90.1
14	6.823	.080	6.743	95.0
Average				91.4

GROUP C

4	11.185	0.149	11.036	99.0
5	10.658	.149	10.509	94.3
8	10.275	.149	10.126	90.8
9	10.945	.149	10.796	96.9
Average				95.2

Here the specimens are divided into three groups—A, B, and C. In group A the current was kept on the specimens during the first period of 429 hours and then switched off, but the specimens were permitted to stand in the soil undisturbed during the second period of 686 hours, after which they were taken out and weighed and the efficiency of corrosion determined. In this case if the initial corrosion due to the electric current tended to accelerate self-corrosion we should expect a higher efficiency of corrosion than if the specimens had been removed as soon as the current was shut off. In group B the specimens also carried current during the first 429 hours, but were removed from the earth, cleaned, and weighed as soon as the current was shut off, and then put back in circuit again. If the self-corrosion is greater due to the initial electrolysis, we should expect that the efficiency of corrosion would be smaller for the first period in group B than was obtained for group A. The table shows that such was the case, although the difference is quite small and may possibly be due to other causes. By cleaning these specimens and putting them back in the same soil in which they had previously run and maintaining the same current flow as before during the second period we

could determine whether there was any marked change in the efficiency of corrosion due to changes in the soil caused by the flow of current. The table shows that there was a marked difference here, the efficiency of corrosion being much lower during the second period than during the first. In group C the specimens were permitted to remain in circuit during both the first and second periods without interruption.

In comparing the results obtained from these three groups it is significant that the highest apparent efficiency of corrosion was obtained when the current was allowed to flow for a time and then removed and the specimen allowed to remain in the earth subjected to the action of self-corrosion during the second period. The next largest apparent efficiency was obtained when the specimens were cleaned and weighed at the ends of the first period immediately after the stopping of the current. The lowest efficiency was obtained when the cleaned specimens of group B were returned to the same earth which had been previously used and again connected in circuit during the second period. Further, group C, which ran continually throughout the first and second periods, showed an intermediate value of corrosion efficiency. These results appear to show that there are two opposing tendencies at work, one of which is to increase the corrosion efficiency, as in group A, due to some cause associated with the flow of current, and the other a tendency to decrease the corrosion efficiency, as in group C, due perhaps to depletion of certain ingredients in the electrolyte. Other experimental data given in this paper indicate that this tendency for the efficiency of corrosion to decrease with time may be due either to the exhaustion of dissolved oxygen or to a loss of moisture by the earth.

The check specimens used in these experiments also show the effect of current flow on the self-corrosion of check specimens placed in the cans along with the anodes. Examining the data for group B under the column headed "Self-corrosion," we find that during the first period the rate of corrosion was less than after the check specimens had been cleaned and returned to the same cans. By comparing the self-corrosion in group A with those in groups B and C the tendency is seen to be the same and even more marked. Further, by comparing the self-corrosion of group B with that of

group C we find that, although the total flow of current is the same, the corrosion is considerably greater in the latter. Since those of group B were removed once and cleaned, while those of group C were not, this result seems to support the theory that the presence of a small amount of initial corrosion tends to stimulate the self-corrosion throughout the remaining period of the test. It should be borne in mind, however, that the figures on which this statement is based are subject to such large variations that they should not be accepted as conclusive until they have been repeatedly verified.

(b) **Depolarizing Effect of Oxygen.**—According to the electrolytic theory of corrosion all iron contains sufficient differences in physical or chemical structure at different points on its surface to set up local galvanic elements which are supposed to be responsible for self corrosion. Under ordinary conditions of self corrosion, therefore, there will be certain points on the surface which will be anode points discharging current into the electrolyte and corroding the iron, and there will also be near by cathode points at which the current reenters the iron. The amount of corrosion which results from these couples will, of course, depend upon the resistance of the local circuit as well as on the effective difference of potential which exists between adjacent points. When current flows in these local paths there is a tendency to form a film of hydrogen at the cathode points which diffuses but slowly, and this not only sets up a counter electromotive force, but it likewise introduces a large amount of additional resistance into the local circuit. In consequence of this the self corrosion may be said to inhibit itself to a very considerable extent. If now we superpose on this specimen an electric current, making the specimen anode, more or less oxygen will be liberated near the surface of the metal which may react with the hydrogen, thus in effect depolarizing the local galvanic elements and permitting much greater self corrosion in the case of a specimen discharging current than in a case of a similar specimen not discharging. This excess of self corrosion would always appear due to the main current flowing and would thus increase the apparent efficiency of corrosion. It is easy to see how this effect could increase the efficiency of corrosion from a low value up toward 100 per cent, although it would not in general tend to make the corrosion efficiency greater than 100 per cent.

(c) **Nonuniform Corrosion of the Iron.**—When iron corrodes it is always with greater or less irregularity. Pits may be formed in which a small hole on the surface may communicate with a large chamber below, and this pitting may pursue such an irregular course as to eat entirely around particles of iron, causing them to fall away from the test specimen. This seems particularly likely to happen in the case of very impure metals, which often exhibit a more or less honeycombed aspect after long-continued corrosion. Since the efficiency of corrosion is always determined from the net loss of weight, any particles of iron that might be dislodged in this manner would be charged against the current, and in this way the corrosion efficiency might easily be made to appear larger than 100 per cent.

(d) **Circulation of the Electrolyte.**—It is well known that if the electrolyte surrounding a piece of iron be kept in constant circulation, the amount of self corrosion which results will be greater than if the electrolyte remains practically still. When an electric current flows through an electrolyte it causes a migration of the ions, which may increase the self corrosion of the iron in a manner analogous to circulation of the electrolyte. Particularly, in the case of an anode there is a tendency for the acid radicals such as Cl, SO_4, etc., to concentrate near the anode surface, and it is well known that liquids containing large amounts of these radicals, particularly the chlorine, produce very rapid corrosion of the iron. Here, again, any excess of self corrosion which would be produced would be charged against the electric current, and a high efficiency of corrosion would result. It is not improbable that any or all of the above-mentioned causes may be operating in certain cases to produce a high efficiency of corrosion. However that may be, it has been definitely established that if a check specimen is embedded in the earth along with the anode the self corrosion will always be much higher than if the check specimen is embedded in the same earth but in a separate vessel. This is true even when ample precautions are taken to shield the check specimens from the flow of electric current. This is shown by the following series of experiments, which is typical of a great many which have been carried out. The anodes were buried in the center of a quart tin can filled with earth, the can itself serving as the cathode. The

check specimen was placed in the earth near the cathode and shielded from current flow by means of a glass shield, semicylindrical in form and of considerably greater diameter and length than the check specimen. The arrangement is shown in Fig. 1. In many of these experiments, in addition to the check specimens placed inside the can, a second check specimen was also placed in the same kind of earth with the same moisture content, but placed in a separate vessel, through which no current passed. A few of these data, which are typical of all, are given in Table 12.

TABLE 12

Effect of Current Flow on Self Corrosion

Check No.	Loss of check with iron carrying current 49 days	Loss of check in separate vessel 83 days	Check No.	Loss of check with iron carrying current 49 days	Loss of check in separate vessel 83 days
	g	g		g	g
7	0.075	0.041	63	0.143	0.063
14	.025	.022	83	.135	.018
21	.091	.025	84	.118	.014
[illegible]	.038	.022			
35	.048	.045	Average..	.092	.034
42	.155	.057			

From this table it will be seen that the average self-corrosion on the check specimens placed in the can carrying current was roughly 2.7 times that on the specimens in the cans through which no current passed, while the time in the latter case was 1.7 times that in the former, thus making the average rate of self-corrosion about 4.6 times as great in the can carrying current as in the one which carried no current. Further, it seems altogether probable from the foregoing discussion of causes of increased corrosion efficiency that the self-corrosion on the anode itself would be considerably greater than that on the check specimen placed inside the same can, so that even though the electrolytic corrosion proper were to take place strictly in accordance with Faraday's law we should nevertheless obtain an experimental result indicating an efficiency considerably greater than 100 per cent.

In view of the foregoing, therefore, it does not appear that we have any reason to suppose that the electrolytic corrosion proper does not take place in accordance with Faraday's law, even though a corrosion efficiency of much more than 100 per cent is indicated. Nevertheless, in computing corrosion efficiency it is proper to charge all of this excess of self-corrosion against the electric current, since in the absence of the current it would not have occurred, and the corrosion directly chargeable to the current includes all of that which results from the passage of the current, whether due directly to the current or to secondary causes brought into action by the current flow.

11. EFFECT OF VERY LOW VOLTAGE

In all of the foregoing experiments, although the current density has often been reduced to quite low values, the voltage impressed upon each pair of electrodes has in general been somewhat high, being of the order of several volts in most instances. This has been due to the fact that the small size of most of the electrodes used gave rise to so high a resistance in the earth that voltages of this order were necessary in order to produce the desired current density. Although there is no theoretical reason why the efficiency of corrosion should vary with voltage, except in so far as it affects the current density, nevertheless it seemed very desirable to carry out a few experiments on very low voltages, particularly below 1 volt, in order to determine whether the efficiency of corrosion would be materially different with such extremely low voltages from what it is on the higher values. Accordingly three cells were made up using tap water as an electrolyte and thin sheet-iron electrodes separated by several sheets of filter paper. This gave very low resistance between the electrodes and made it possible to secure sufficiently large current on much lower voltages than had been possible in the case of specimens buried in soil. One of these cells was run on a constant potential of 0.1 volt, another on 0.6 volt, and the third at 1 volt. Current measurements were made at frequent intervals and the ampere hours determined. The results are shown in the table following.

TABLE 13

Low Voltage Test

[Area of anode, 47.47 square centimeters; average natural loss of anode, 40 mg]

Plate No.	Loss total	Electrical loss	Theoretical loss	Corrosion efficiency	Current density (mil. amps. cm^2)	Voltage
1	0.496	0.456	0.467	97.7	0.051	1.0
2	.153	.113	.127	89.0	.014	.6
3	.062	.022	.024	91.7	.003	.1

It will be seen by reference to this table that the efficiencies of corrosion are comparatively high, being highest in the case of the 1-volt cell and lowest in the case of the 0.6-volt cell and intermediate in the case of the 0.1-volt cell. The current densities are given in the table and are seen to be extremely low, the lowest being but 0.003 of a milliampere per square centimeter. These results show quite clearly that there is no reason to expect that the corrosion efficiency changes materially at any critical value of voltage within a range that is of any practical consequence in the negative return of street railway systems.

III. EARTH RESISTANCE

The foregoing experiments show what may in general be expected under different conditions as to the discharge of current from iron electrodes buried in soils. In practice, however, when investigating electrolysis conditions, we are not dealing with known conditions of current flow, since it is in most cases impracticable to measure directly leakage currents at any point in the soil without resorting to measures that are too tedious and expensive for most work. We have, on the contrary, certain easily determined voltage conditions throughout the negative railway return system, and hence, in order to properly interpret the data above presented relating to laws of corrosion, it is necessary to take into consideration the effect of earth resistance on the stray currents that may be carried by the pipes and discharged by them into the earth under known conditions as to potential differences in the network. It is not the purpose of this paper to go into detail in regard to the matter of earth resistance, as this is to be

treated somewhat fully in another paper by the authors in a publication of the Bureau of Standards. The great importance of the subject of earth resistance, however, in relation to electrolytic corrosion in soils makes it desirable to present here very briefly a few fundamental principles in regard to the resistance of soils and its relation to stray-current electrolysis.

It is obvious that if the soil surrounding the pipe network possessed infinite resistance there would be no trouble from electrolysis, since in that case no stray current could leak off of the tracks and hence find its way into the pipes. On the other hand, if the earth possessed zero resistance, we would also have no electrolysis, since in that case the earth would short circuit the pipes and prevent them from taking up the stray currents. Somewhere between these two extremes we will obviously have a value of earth resistance which in any given case would produce a maximum of electrolysis trouble. The value of this resistance required to give a maximum electrolysis undoubtedly varies greatly with conditions, such as geometrical form of the pipe and track networks, kinds of joints used in pipes, size of pipes, resistance of rail return, and numerous other factors. We feel confident, however, from observations made under practical conditions that in most if not all cases the resistance of the earth will be found much higher than that required to produce maximum electrolysis, so that in general we may expect the electrolysis to be greater the lower the resistance of the earth. With a view of giving an idea of what may be expected in the way of earth resistance in practice, we present below a summary of some investigations which we have made in regard to variation of earth resistance with varying conditions, and following that we have given the results of a considerable number of earth-resistance measurements made on a variety of soils taken from widely scattered sources. In making these earth-resistance measurements several different methods were used, in some of which the earth was measured in place without being disturbed, while in other cases the samples were taken to the laboratory, packed in glass cylinders, and the resistance measured between plastic amalgam electrodes pasted on the ends of the cylinder, the voltmeter-ammeter method with alternating current being used. In a good many cases both

methods were used and the results were found to check in a very satisfactory manner. In making the earth-resistance measurements in place two excavations were made side by side to a depth of several feet, leaving a portion of undisturbed earth several inches in thickness between the two excavations. The sides of this undisturbed portion were made approximately parallel and fairly smooth, and small electrodes a few inches in diameter placed on the opposite sides. These electrodes were then surrounded by guard rings of sufficient diameter to assure practically parallel lines of current flow between the two electrodes. The resistance of the earth between the electrodes was then measured by means of the voltmeter-ammeter method as in the laboratory, alternating current being used for the purpose. In making these measurements care was taken to keep the electrodes and the guard rings not only at the same potential, but also to see that there was no displacement of phase between the emf's applied to them.

In making the tests in the laboratory preliminary experiments showed that much more satisfactory results could be obtained by compressing the earth in the testing machine to such a point that further increase in pressure caused practically no variation of resistance. It was found, and will be shown by the curves below, that with increase of pressure a point is soon reached beyond which the resistance varies but slightly with further increase in pressure. Careful comparison of results obtained by first measuring the resistance in place in the ground, and later in the same earth in the laboratory, indicated that they were practically the same whichever method was used, and since the method of measuring the resistance in the laboratory was so much more rapid and convenient this method was used for the great majority of of measurements that are presented below.

1. EFFECT OF MOISTURE CONTENT ON EARTH RESISTANCE

Moisture content is one of the controlling factors in earth resistance. In Table 14 are given a series of resistance measurements taken on a sample of red-clay soil with varying moisture content, which may be regarded as more or less typical.

TABLE 14

Relation Between the Amount of Moisture in the Soil and its Specific Resistance

Per cent moisture (in terms of dry earth)	Specific resistance (ohms per centimeter cube)	Per cent moisture (in terms of dry earth)	Specific resistance (ohms per centimeter cube)
5.0	2 340 000	44.5	4725
11.1	237 400	55.6	4870
16.7	13 880	56.7	5197
22.2	6835	77.8	5045
33.3	5400		

For making each measurement a new sample of thoroughly dry earth, dried at 105° C, was taken and the required amount of moisture added, the percentage of moisture being expressed in terms of the dry earth. It will be seen that above about 22 per cent of moisture the resistance remains practically constant, but below this value the resistance rises very abruptly with decrease of moisture content, and at 5 per cent of moisture the resistance has risen to considerably over 400 times its value when the soil is saturated. This shows that the actual current flow to and from a pipe embedded in soil is dependent in vastly greater degree on the moisture content than on the potential difference between the pipe and surrounding structure, and points to the fact that a potential difference which might be perfectly safe in a high and well-drained locality might be sufficient to give rise to a great deal of damage in a low and damp locality. This tendency has of course been well recognized, but it has not been given the consideration which it deserves. Cases frequently arise in which this fact might well be treated as an important factor in determining the location of a railway substation, and particularly the points at which insulated radial return feeders might best be connected to the tracks.

Another important practical aspect of this change in resistance with moisture content is its effect on the distribution of potential drops throughout the negative railway return area. Since the various parts of the pipe systems are buried at different depths and are very irregularly located with respect to the tracks, it is

evident that changes in the moisture content with depth will exert a marked influence on the distribution of the resistance in the path of the leakage current, which in turn will greatly affect both the magnitude and distribution of the potential gradients through-

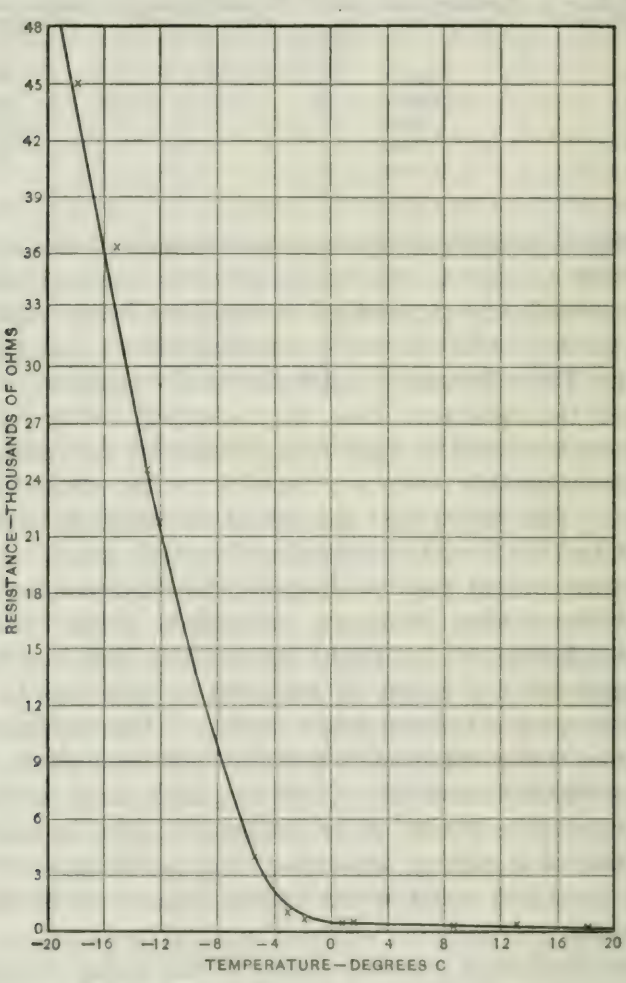

Fig. 8.—*Effect of Temperature on Earth Resistance*

out the system. For this reason not as much reliance should be placed on voltage surveys made at extremely wet, and more especially at very dry periods, as on those taken under more nearly average moisture conditions.

2. EFFECT OF TEMPERATURE ON EARTH RESISTANCE

The effect of temperature on the resistance of soil was determined throughout the range from about 18° C to −18° C (0 to 65° F). For this purpose a moist soil was used and was placed in a vessel surrounded by an ice chamber in which a mixture of ice and salt was placed, and the whole was allowed to stand until the temperature had reached about −18° C, the resistance being measured from time to time by means of electrodes which were embedded in the sample of earth and brought out by rubber-covered leads. The temperature of the earth was taken at the same time each resistance measurement was made, an ordinary mercury thermometer inserted in the center of a hollow electrode being used. The results of these resistance measurements as a function of temperature are given in Table 15 and are plotted in Fig. 8. By reference to the curve it will be seen that the resistance varies throughout very extreme ranges, even within the ranges of temperature variation that commonly occur in this country. Above freezing the resistance variation is much less marked, but even here we find that the resistance at 0° C is is approximately 2½ times its value at 18° C. At about the point at which the soil water begins to freeze there is a tremendous increase in the temperature coefficient of resistance, and as the temperature becomes lower the resistance rises enormously, and at −18° C the resistance is seen to be over 200 times as great as at 18° above zero.

TABLE 15

Effect of Temperature on Resistance of Soil

[Soil No. 32; moisture, 18.6 per cent; specific resistance at 20°, 6260 ohms/cm³]

Temperature	Resistance	Temperature	Resistance
°C	Ohms	°C	Ohms
18.0	224	− 3.0	1185
13.0	286	− 5.5	4340
8.5	398	−12.0	21 700
1.5	458	−13.0	24 600
1.0	462	−15.0	36 200
0.0	542	−18.0	45 000
−2.0	940	−19.0	48 900

This enormous variation of earth resistance with temperature is of considerable practical importance and indicates that in moderately cold weather such as prevails in the northern cities comparatively little trouble from electrolysis may be expected. This is due not primarily to the higher resistance of the earth immediately surrounding the pipes, since the pipes are usually located at a sufficient depth so that the temperature of the earth immediately surrounding will not reach the lower values used in this experiment. The real reason for the diminution of electrolysis trouble with the fall in temperature is the reduction of leakage current from the rails. It will be evident that when the ground is frozen even but a few inches deep the resistance of the earth immediately surrounding the rail is enormously increased, and the leakage of stray currents into the earth is thereby correspondingly reduced. And since the rise in resistance with even a few degrees of frost may be manyfold, it is apparent that but a thin layer of frozen earth about the rail would be necessary in order to produce a very marked increase in the total resistance of the path of the leakage current. This reduction in electrolysis troubles in cold weather due to increase in resistance of the earth is further augmented by the increase of the conductivity of the rail return which takes place at the lower temperature, which may amount to as much as 15 or 20 per cent, and is sufficient as a rule to compensate for the increased load which usually prevails during the cold period.

It should also be pointed out here that the effect of variations in temperature with depth on the resistance of earth will have an effect on the distribution of potential gradients in the earth very similar to variations in moisture content referred to above. For this reason it is preferable not to make voltage surveys at times when extremely low temperatures prevail.

3. EFFECT OF MECHANICAL PRESSURE ON EARTH RESISTANCE

Of considerable interest, although of much less practical importance, is the effect of mechanical pressure on the electrical resistance of earth. As already stated, when pressure is applied to a sample of earth its resistance is but little affected, as a rule, after a certain relatively low value of pressure is reached. This is shown in Fig. 9, which gives resistance-pressure curves for a num-

ber of different soils from various sources. The range of pressures here are for the most part between 20 and 1000 pounds per square inch, and the variations in resistance between these limits are surprisingly small. Numerous measurements of the resistance of

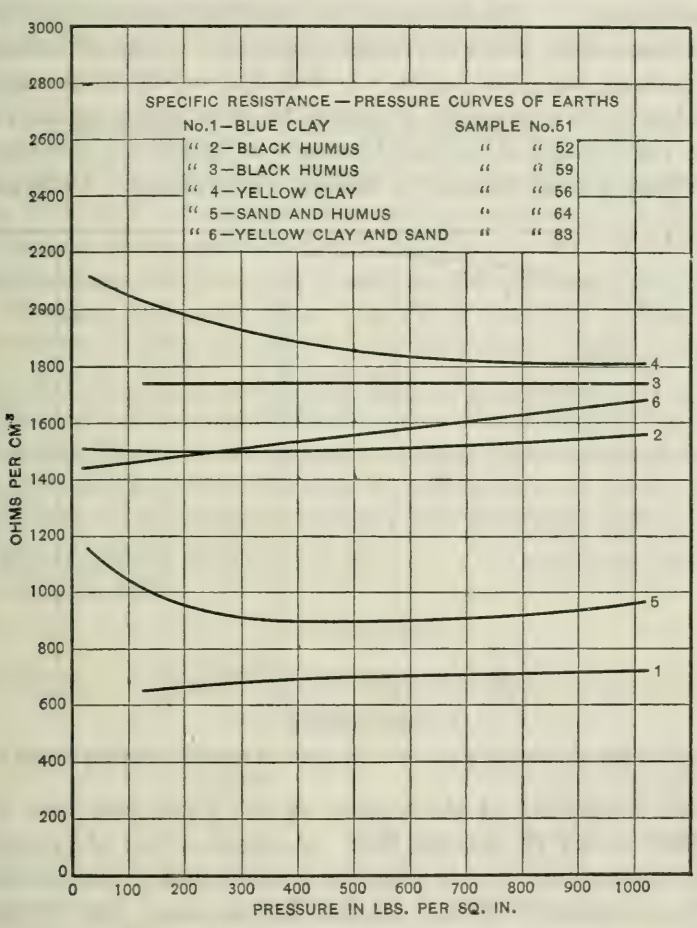

Fig. 9.—*Effect of Mechanical Pressure on Earth Resistance*

earth 2 or 3 feet below the surface before being disturbed, using the guard-ring method, and subsequent measurements of the same earth in the laboratory under pressure show that the resistance at a few hundred pounds' pressure per square inch is substantially the same as the undisturbed earth.

4. OTHER FACTORS AFFECTING CURRENT FLOW

There are other factors also which affect the resistance of soils, such as its mechanical properties and chemical constituents, and these may have an important bearing on current flow to and from the buried pipes. The character of the street railway roadbed is also an important factor in determining the extent of leakage of stray current into the earth. A well-drained rock or concrete roadbed may in general be expected to offer much higher resistance to the leakage of current than one in which the construction is such that a large amount of moisture is retained. Polarization

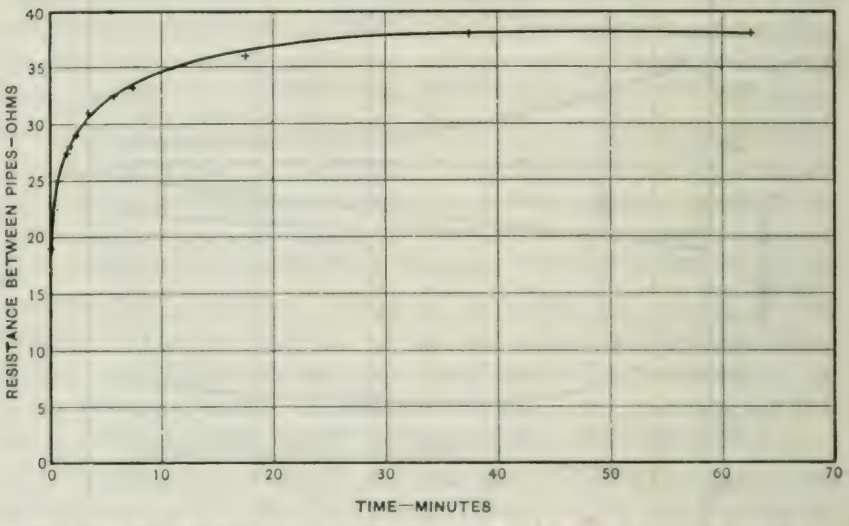

Fig. 10.—*Effect of Polarization and Film Resistance on Resistance Between Buried Pipes*

and film resistances at the surface of the pipes may also be an important factor in current flow. As soon as an electromotive force is applied to a buried pipe the current flow drops off rapidly with time, especially during the first few minutes, due to the setting up of counter emf's and the formation of film resistances. The extent to which this may occur in some cases is shown in Fig. 10, which shows the effective resistance as a function of time after the application of an emf of about 6 volts between two short lengths of cast-iron pipe buried about 12 feet apart. From this it will be seen that the initial resistance of about 18 ohms has

practically doubled within half an hour after the emf is applied, and after that the resistance remains practically constant. In this case the effect of the polarization and film resistance is practically as great as the total soil resistance between the pipes. These results were obtained when the soil was very wet, and it is probable that in a comparatively dry soil the effect would have been less marked.

5. RESISTANCE OF SOILS FROM DIFFERENT SOURCES

In order to give an idea of the order of magnitude of the resistances that may be expected in practice, together with the range of variation of the same, we give herewith a table of resistances of soils taken from various points in the cities of Philadelphia and St. Louis and other cities. In all of these the specific resistance of the soil is measured with the same moisture content which it had when first taken from the ground, and all were measured at about one temperature. The soils from each city were taken from widely scattered points and represent a great variety of different kinds of soils, as will be evident from the brief description. The moisture content was determined in each case and is given along with the other data. The results are shown in the following table:

TABLE 16

Specific Resistance of Soils

PHILADELPHIA SOILS

No.	Character	Moisture	Specific resistance
		Per cent	Ohms—cm³
1	Moist gray clay	11.7	651
2	Moist yellow clay	14.8	3850
3	Moist blue clay	16.1	3036
4	Near dry red sand	7.6	2700
5	Moist red clay	17.4	8820
6	Nearly dry mica schist	4.7	156 400
7	Nearly dry gray clay	16.2	5930
8	Nearly dry clay rock and cinders	17.9	595
9	Moist blue clay and gravel	13.1	2830
10	Moist blue clay	15.3	1605
11	Moist yellow clay	17.2	5340
12	Moist yellow clay and sand	13.4	6280

TABLE 16—Continued

Specific Resistance of Soils—Continued

PHILADELPHIA SOILS—Continued

No.	Character	Moisture	Specific resistance
		Per cent	Ohms—cm³
13	Wet gravel	11.0	24 550
14	Wet humus and clay	9.5	2600
15	Moist clay sand cinders	17.4	2060
16	Damp disintegrated schist	12.9	12 100
17	Wet clay cinders gravel	16.8	5000
18	Moist yellow clay	19.4	4825
19	.....do	17.3	3820
20	Moist red clay	19.3	21 200
21	Moist yellow clay	15.6	25 900
22	Moist red sand and clay	15.7	13 700
23	Moist clay cinders sand	13.7	1494
24	Moist clay and sand	20.0	821
25	.....do	18.7	1774
26	Damp clay and humus	16.7	2490
27	.....do	16.2	2585
28	Near dry disintegrated schist	0.3	610 000
29	Damp yellow clay	16.8	2250
30	Moist yellow clay	18.5	2455
31	Saturated clay and cinders	23.8	4410
32	Moist clay and sand	18.6	6260
	PITTSBURGH SOILS		
33	Damp sand	13.4	4506
34	Moist yellow clay	16.5	2819
35	Moist clay and humus	20.5	2300
36	Blue clay	26.5	14 025
37	Moist gray clay	26.3	619
38	Damp sand	13.0	1335
39	.....do	10.2	8709
40	Loam and cinders	21.8	1074
41	Near dry sand	12.3	2908
	ERIE SOILS		
42	Moist clay and gravel	6.0	18 080
43	Clay coal gravel	16.7	1796
44	Wet blue clay	19.3	3779
45	Moist blue clay and sand	11.9	3080
46	Moist gravel	5.7	14 025
47	Wet blue clay and sand	19.6	2462

TABLE 16—Continued

Specific Resistance of Soils—Continued

ST. LOUIS SOILS

No.	Character	Moisture	Specific resistance
		Per cent	Ohms—cm³
50	Wet clay	20.4	600
51	Blue clay	21.1	700
52	Moist virgin soil	20.8	1500
53	Moist yellow clay	21.5	1250
54	Yellow clay	19.0	1800
55	.....do	.....	1600
56	.....do	21.1	1800
57	.....do	22.8	1400
58	Yellow clay	21.3	1400
59	Virgin black soil	21.2	1700
60	Yellow clay	16.0	1800
61	.....do	23.4	990
62	.....do	18.4	700
63	.....do	21.9	950
64	Sand and humus	17.8	925
65	.....do	20.0	900
66	Blue clay	22.0	470
67	Virgin yellow clay	19.1	1450
68	.....do	22.5	484
69	Yellow clay	22.0	700
70	Virgin yellow clay	20.0	1700
71	Virgin soil	22.9	840
72	Yellow clay	23.3	900
73	Blue clay	26.1	400
74	.....do	19.1	600
75	.....do	24.2	830
76	Moist blue clay	23.1	500
77	Near dry yellow clay	16.4	1100
78	Blue clay	17.1	650
79	Yellow and blue clay	26.9	600
80	.....do	19.7	820
81	Blue clay	20.0	750
82	Clay and loam	19.2	1450
83	Sandy clay	19.5	1600
84	Yellow clay	22.6	1200
	APOLLO, PA., SOIL		
48	.....	30.5	1796
	ALBUQUERQUE, N. MEX., SOILS		
85	.....	15.3	43 960
86	.....	11.1	59 475
87	.....	11.9	41 908

TABLE 16—Continued

Specific Resistance of Soils—Continued

WASHINGTON, D. C., SOILS

No.	Character	Moisture	Specific resistance
		Per cent	Ohms—cm³
88	Air-dry red clay	4±	2 340 000
89	Near dry	10	14 660
90	Moist loam	20	8729
91	Wet yellow clay and sand	30	41 490
92	Wet humus, clay, and sand	30	24 060

An examination of this table reveals some striking differences in two particulars: In the first place, the specific resistances found in St. Louis show a much greater degree of uniformity than those found in Philadelphia. The extreme range of values of specific resistance for St. Louis earths is between 400 and 1800 ohms per centimeter cube, while for Philadelphia the range is between 595 and 610 000 ohms per centimeter cube. The other chief point of difference is the magnitude of the mean value of resistance, the average value of the specific resistance for all the samples taken in St. Louis being 1053 ohms, while the average for the Philadelphia samples was 28 750 per centimeter cube, the latter being over 27.3 times the former. It should be noted, however, in making this comparison that the high average for Philadelphia is due to a large extent to the abnormally high resistance of two samples containing large quantiites of mica, one of which had a specific resistance of 156 400 ohms and the other 610 000 ohms. If these two are eliminated, the remaining 31 specimens show an average for Philadelphia of 5885 ohms per centimeter cube, which, however, is still over 5.6 times the value for St. Louis. It is quite probable that this difference is such as to prove an important factor in the electrolysis situation in the two places.

IV. CONCLUSIONS

The following are some of the more general conclusions that may be drawn from the experimental data presented in this paper:

1. The current density has a marked effect on efficiency of corrosion of iron in soils, the efficiency of corrosion being, in general, greater the lower the current density. In saturated soils

the corrosion may vary between 20 per cent and about 140 per cent for the range of current densities between 5 milliamperes and 0.05 milliampere per square centimeter.

2. Moisture content in the soil also has a marked effect on efficiency of corrosion, the corrosion efficiency being in general greater with increasing moisture content up to saturation of the soil. Beyond this point increased moisture content has comparatively little effect.

3. Temperature changes within the limits commonly met with in practice have no important effect on corrosion efficiency.

4. The depth of burial of pipes has no direct effect on corrosion efficiency provided other conditions remain constant. In practice, however, the moisture content, current carried by the pipes, and various other factors which affect corrosion efficiency will vary with depth, so that indirectly differences due to depth may be noted.

5. The amount of oxygen present has no appreciable effect on the efficiency of corrosion in the case of iron immersed in liquid electrolyte.

6. Corrosion efficiency of iron embedded in earth is always greater in open vessels than in sealed vessels.

7. The amount of oxygen present has a marked effect on the end products of corrosion. If the corrosion is rapid and the supply of oxygen small, there will be a preponderance of magnetic oxid, while if the rate of corrosion is low and the supply of oxygen abundant the ferric oxid will predominate. Owing to the fact that the supply of oxygen around pipes buried in earth is always more or less limited, the character of the oxids formed gives some indication as to the rate of corrosion, and thus indirectly the cause of the corrosion, if local conditions are properly considered.

8. There is no material difference in the efficiency of corrosion shown by the various kinds of iron commonly used in the manufacture of underground pipes.

9. The fact that a given chemical tends strongly to inhibit either self-corrosion or electrolytic corrosion in liquids is no indication that it will materially retard electrolysis of iron embedded in soils.

10. Pitting of iron embedded in soils is affected not only by a nonhomogeneous condition of the iron or soil, but also by the chemicals contained in the soil.

11. The efficiency of corrosion was found not to be a function of the voltage except in so far as the current density may be affected. Voltages as low as 0.1 and 0.6 volts showed practically the same efficiency of corrosion as 5 to 10 volts or higher.

12. Corrosion tests on a large number of different kinds of soil from widely different sources with average moisture content and moderate current density indicate that corrosion efficiencies between 50 and 110 per cent may usually be expected under most practical conditions.

13. The resistance of soils varies throughout a very wide range with variations in moisture content, the resistance of the comparatively dry soil being of the order of several hundred times the resistance of the same soil at about saturation. Above saturation, increase in moisture content has but little effect on the resistance of the soil.

14. Because of the great variations in resistance of earth with moisture content, voltage surveys should not be made at times when the earth is extremely dry.

15. The resistance of the soil varies greatly with temperature within the ordinary range encountered in practice. In the case of the soil tested the resistance at 18° below zero centigrade was over two hundred times as great as at 18° above zero centigrade. Even at about freezing temperature the resistance will be several times that at summer temperatures. This not only has an important bearing on the magnitude of the electrolysis trouble that may occur at different seasons, but it also indicates that where practicable voltage surveys should not be made when extremely low temperatures prevail.

16. The experimental results given in this paper have an important bearing on the subject of electrolysis mitigation through the limitation of voltage drop in the negative return. For some years the chief means of preventing trouble from electrolysis in certain foreign countries has been the limitation of the permissible voltage drop between any two points on the return circuit. In some places the limit has been placed on the maximum voltage during

peak load, whereas in other cases the average voltage for 24 hours has been the determining factor. It will be evident that if the total amount of damage which results is proportional to the average current, then the limitation of the average voltage would be more logical than the limitation of the peak-load voltage, since in the former case the cost of meeting the voltage limitation in any given case would be proportionate to the danger involved irrespective of the station load factor; whereas if the voltage at peak load is the determining factor the cost of complying with the requirements depend not only on the danger involved but on the load factor of the system, and the poorer the load factor the greater its cost will be. It appears from the data presented in this paper that the rate of damage does not increase as fast as the voltage increases, because of the tendency toward lower corrosion efficiencies at higher current densities. This indicates that, with a given average all-day current the actual amount of electrolysis that would occur would be less with a bad load factor than with a good load factor, and hence points to the undesirability of penalizing a high peak of short duration. It would appear more logical, therefore, in so far as the damage itself is concerned, to make the average all-day voltage the basis of the limitation rather than the voltage at time of peak load.

In conclusion, the authors wish to acknowledge their obligation to their colleagues, Mr. O. S. Peters and Dr. H. E. Palmer; to the former for valuable cooperation in the development of the electrolytic method for cleaning anodes which was used throughout this investigation, and also for a large amount of work on the measurement of earth resistances; to the latter for the chemical analyses of soils and the carrying out of experiments on the effect of oxygen on the end products of corrosion.

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METHODS OF MAKING ELECTROLYSIS SURVEYS

BY

BURTON McCOLLUM, Electrical Engineer

and

G. H. AHLBORN, Assistant Physicist

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METHODS OF MAKING ELECTROLYSIS SURVEYS

By Burton McCollum and G. H. Ahlborn

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Part 1.—INTRODUCTION

I. DEFINITION AND SCOPE OF PAPER

The subject of electrolysis surveys deals with the various methods or types of measurement employed to determine the danger to underground pipes and cables and other structures due to the flow of stray electrical currents, the extent of damage already produced by them, and the proper mitigative measures that should be applied for reducing future trouble in particular cases. It is the purpose of this paper to discuss the methods of determining electrolysis conditions; of collecting data upon which the design of mitigating systems may be based, including a discussion of the measurements to be taken; the characteristics of the instruments best adapted to the requirements; the procedure to be followed; the recording and arrangement of the data; and to a certain extent the interpretation of the results. This discussion is based on the experience and observation of the engineers of the Bureau of Standards and others who have been engaged in this work, both in this country and abroad. It is hoped that the paper will enable those who are less familiar with this work to proceed more efficiently in carrying out a survey, avoiding certain errors and unnecessary measurements, and that it will assist materially in establishing a better understanding of the significance of the results obtained.

It should be emphasized here, however, that in general no two electrolysis surveys will be conducted in exactly the same way, so that it is not possible to lay down a definite and complete program. The procedure prescribed in this paper is intended to cover those measurements most frequently made and to describe methods that have been found suitable for making them. The kind and character of the readings taken, and to a certain extent the details of procedure to be followed will vary so much with individual conditions that much reliance must be placed on the judgment of the person conducting the tests. In fact, the proper procedure during a large part of the survey will depend in large measure on the results obtained in the preliminary tests. In general, therefore, it is important that investigation of electrolysis conditions be undertaken under the direction of a competent engineer very familiar with the method of procedure in securing test data as well as experienced in interpreting the results of such tests.

With the rapid growth in the extent of trolley lines and the traffic carried by them, and the agitation for the protection of underground piping systems and other underground structures against electrolysis, the importance of and interest in this subject have increased tremendously. The damage due to stray currents has followed so closely upon the construction and operation of trolley lines and is so generally a phenomenon accompanying the operation of such lines that it may be considered as a problem of street railway engineering. Only a few years after the introduction of electric railway systems in 1884, serious corrosion of pipes occurred in certain places and efforts were made to determine the cause and eliminate the trouble. Electrolysis from other causes than street railway stray currents is not unknown, but the instances are so infrequent and the damage so small as to deserve only a passing comment for the purpose of pointing out that some grounded circuits, of which the Edison three-wire system is the most common example, may do damage to sheaths or pipes even if only small differences of potential exist between the different grounded points.

II. PURPOSE OF ELECTROLYSIS SURVEYS

By means of proper measurements it is possible to determine with sufficient definiteness for most purposes the extent and location of the areas in which the pipes and other structures are in danger and the degree of seriousness of the trouble. The cause of the damage in progress, whether due to stray currents or natural corrosion by soil, cinders, or organic matter, can generally be ascertained, and in case of electrolytic corrosion the source of the current can generally be definitely determined. The various factors connected with the pipe systems, which tend to aggravate electrolytic damage, such as infrequent local discontinuity or high resistance in the pipe systems, unusually low-resistance soil or the use of certain methods of mitigation not adapted to existing conditions, may also be detected. Defects in the railway return systems which tend to give rise to electrolysis troubles, such as poor rail joints, infrequent cross bonds, insufficient conductance in the negative return, improper use of such conductance, or too long feeding distances, may be determined.

III. CLASSES OF SURVEYS

In the following discussion several classes of surveys are recognized. The first is what may be called a complete electrolysis survey, which is made not only for the purpose of determining the extent and location of the danger from electrolysis, but also with the view of determining the proper procedure to be followed for the permanent mitigation of the electrolysis trouble. The second embraces such surveys as would usually be made by a pipe or cable owning company solely for the purpose of determining whether existing conditions are satisfactory and differs from the former mainly in that most of the information with respect to the railway system is not required, and fewer electrical measurements are taken, the number and character of those obtained depending on the thoroughness with which the survey is to be carried out. A third class of survey, which needs little discussion, however, is one made to determine whether ordinances or regulations governing electrolysis conditions in a municipality are being complied with. Such surveys are usually made periodically, the periods usually varying from three months to a year. In general, in such surveys those quantities are measured which are specifically limited by the ordinances or regulations which are in effect in the locality in question. In this paper there is discussed the various types and classes of measurements and the general character of the information that should be sought in carrying out a complete electrolysis survey. No attempt has been made to outline briefer classes of surveys, since the data required for these will vary so much with individual circumstances that they will have to be determined by the engineer in charge of the work. The procedure, however, in obtaining the data which the plan of the survey calls for will not be materially affected by the omission of certain tests which would be called for by the complete survey.

Part 2.—PRELIMINARY DATA

I. DATA REGARDING PIPE AND CABLE SYSTEMS

In making electrolysis surveys a considerable amount of preliminary data are usually necessary. It is of first importance to gather all evidence regarding the character, extent, and location of known damage to underground structures. This evidence may usually be obtained from the companies operating the water, gas,

telephone, and other underground systems, but even though these companies can give no direct testimony as to injury of underground structures this does not always indicate that no damage exists. The data on the pipe and cable systems should include the location of the mains and railway tracks shown on a map. The type of joints used, and the kind of pipe material—for example, cast iron, steel, etc.—should be determined. Where current measurements are desired, the size and other data for definitely determining the cross section and conductivity of the pipe sections should be given for the particular sections on which current measurements are to be made.

II. DATA REGARDING RAILWAY SYSTEMS

As regards data on the railway system the following should be determined:

1. The character of the service, whether city, suburban, or interurban. This will have a bearing on the schedule, momentary variation in load on different lines, and load factor.

2. Physical data on railway systems, such as rail weights, types of bonds and joints used, and roadbed construction.

3. The practice of the railway company in regard to frequency of cross-bonding, bond maintenance, and bond testing.

4. Load curves are necessary for the interpretation of the data in order to reduce short-time readings to all-day or other average values. Where the load varies considerably in different sections of a power-house feeding area, it may be necessary to get the load curves on different feeders as well as the total power-house load curve.

5. Where a survey is made with the ultimate purpose of correcting electrolysis conditions by applying some method of mitigation, it will also be necessary to secure complete data on the magnitude and distribution of load, the generating and substation feeder systems, frequency of schedule, and probable future demands of traffic.

Much of the above data can be most conveniently shown on a map of the railway system which would include location of tracks and return feeders, weight of rails, and location of cars based on schedules and running speeds and the average current per car.

Part 3.—ELECTRICAL MEASUREMENTS

In discussing the electrical measurements required for a complete electrolysis survey they have been divided into three general classes, namely, voltage surveys, current surveys, and miscellaneous readings. In the ensuing discussion not only the methods and instruments best adapted to the work but the purpose of the measurements and the interpretation of the results will be dealt with.

I. VOLTAGE SURVEYS

The number and character of the potential readings required depend on the information wanted. As was pointed out in a preceding paragraph, the readings taken depend on the nature and thoroughness of the investigation to be made, and this is emphasized here because a number of potential measurements are described which, although often useful, would be unnecessary in many cases. For example, simple preliminary surveys to indicate where damage has occurred would hardly require extensive over-all potential measurements or measurements of potential gradients. On the other hand, if it is necessary to redesign the railway return to take care of electrolysis conditions, more complete observations of potential conditions are requisite, and in certain experimental work one finds it necessary to get data bearing on every phase of the problem. The voltage surveys are here divided into three main classes: (1) Over-all potential, (2) potential gradient, and (3) potential difference measurements. The latter term applies to potential measurements taken between different structures, such, for example, as between water pipes and lead cable systems, or between pipes and railway tracks.

1. OVER-ALL POTENTIAL MEASUREMENTS

(*A*) **Definition.**—The expression "over-all potential" is here applied to the difference of electrical potential existing between the point of lowest potential in any feeding district and the points of approximately highest potential on or near the various branches of the railway system. They thus reveal the maximum differences of potential which exist in the earth or in the rails, which are the immediate sources of the stray current. A power house has a feeding area at all points of which the ground and rails are positive to the negative bus bar, which is almost universally the grounded or return side. The difference of potential between the

negative busses of two stations and a point on the tracks is the algebraic sum of the potential drops between that point and the negative busses of the two stations, making it possible that either station bus may be positive to the other. For the same reason the over-all potential between any bus and a point in another power-house area consists of two or more components of different signs and the bus may even be positive to that point. However, the concentration of current as it approaches a power house with the usual type of return system—that is, designed with converging and a constantly decreasing number of tracks and the current itself constantly increasing—produces large potential gradients in close proximity to the station and all of the busses are therefore negative to a very large per cent of all the railway area. The tendency for leakage from the rails, which is one of the fundamental factors, under average conditions is determined in large degree by the maximum differences of potential existing between points within any feeding area rather than between points lying in different feeding districts.

(*B*) **Importance of Over-All Potential Measurements.**—The importance generally attached to over-all potential measurements as an indication of electrolysis conditions is indicated by the fact that all laws and regulations that have thus far been adopted for reducing electrolysis troubles have recommended the limitation of the over-all potential drops to some definite and relatively low value. Such limitation has been required or recommended in regulations in effect in Great Britain, in various cities on the Continent, and in a number of cities in America.

In all laws and regulations that have up to the present time been adopted, so far as we are aware, the over-all potentials and potential gradients have been specified as those taken between various points on the railway tracks. This is true of the various European ordinances as well as those adopted in this country, and such limits have proven quite successful, particularly in Europe, in relieving the electrolysis troubles. There is much to be said, however, in favor of limiting potential drops in the earth or on pipe networks rather than on the railway tracks. Such voltages afford the most accurate criterion of all as to the actual danger of underground structures and would also prove more advantageous to the railway companies, since if potential drops in the earth or on the pipes are made the subject of limitation, higher voltages could be allowed on those tracks having a high resistance to earth.

Under this plan low voltages in the tracks would be required only where most needed, and railway companies would be encouraged to so construct the track as to give a high-leakage resistance to ground. If, however, the voltage drop in the track is limited by regulations, any construction of roadbed that would reduce leakage would increase the current flowing on the track, thereby increasing the voltage drop and thus increasing the difficulty and cost of complying with the regulations. On the other hand, if the voltage drop on the pipes is made the basis of the regulation, the railway companies would profit by any construction which tends to reduce the leakage instead of suffering by it, as in the case where voltage drops in the tracks are limited. If this plan were adopted, it would be necessary to prescribe lower voltage limits than would be applicable to tracks in order to secure the same freedom from electrolysis.

Over-all potential measurements, when interpreted in the light of other conditions to be discussed later, afford a valuable index of electrolysis conditions generally. The over-all potential is also a quantity which lends itself to easy and ready determination. In cases of reported damage these measurements reveal whether the railway systems are seriously at fault, and what lines or sections are most concerned. When taken in conjunction with certain load data they permit the calculation of the negative power losses, and they also yield valuable information bearing on the desirability of rearranging the feeding areas. When studied with due regard to the character and location of the railway lines and power houses and the distribution of the loads, the probability of too high a current density in the return, local high resistance in the return, or too great feeding distances can be determined. It seems desirable, therefore, in most cases that the over-all potential measurements be the first step in a complete electrolysis survey.

(*C*) **Instrument Leads for Taking Over-All Potential Measurements.**—Since the points between which the potential is to be observed are quite widely separated, the problem of bringing lead wires from these points to the voltmeter is one of considerable importance. For spans of 1000 feet or less, leads on the ground may be used, but the consideration of such measurements more properly belongs to the discussion of potential gradients. Lines may be strung on poles or on the trolley span wires and be used for this purpose solely. This may be done when it is desired to get continuous records for long periods of time, probably at points

which represent the maximum over-all potentials and where records are required by ordinance or needed as evidence, and in some cases it may be found more economical than renting telephone wires. For temporary use, however, as when surveys are made only at infrequent intervals, the use of telephone lines which are already in place is most convenient, there often being idle pairs which are especially suited to the purpose. They usually extend to every part of a city, and by trunking through the various exchanges any two points may be connected to the voltmeter. Since the over-all potentials seldom exceed from 10 to 30 volts the telephone cables are in no danger from voltage breakdown. We have never experienced any disturbance of the telephone service

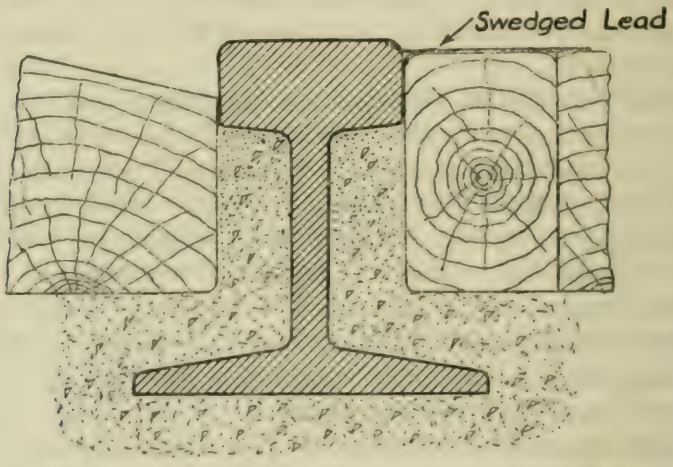

FIG. 1.—*Method of making permanent connection to rail*

due to the use of these wires either from noises in parallel lines or damage to the circuits. When the number of idle pairs available for over-all voltage measurements in a certain district is limited the pairs may be split, using one wire to connect to each point. Where plenty of idle pairs are available, however, it is best to connect the two wires in parallel, thereby reducing the resistance of the leads, which in long lines may become considerable.

The point of lowest potential on the rails or pipes in any power-house area is the logical place for connecting the lead from the negative terminal of the instrument. This will usually be the point on the rails nearest the negative bus, but this is not necessarily so, especially when insulated negative feeders are used. Since the other points will usually be compared to this most negative one, the contact and connection to the latter should be

made quite permanent in character by one of the methods described below.

To reach the rails at outlying points, a connection must be made between the rail and the lead wires. If only a short-time reading with an indicating instrument is desired, a workman may make contact during the reading, but if a longer record of voltage conditions is necessary, or if the reading is to be frequently repeated, a lead protected from traffic must be permanently attached to the rail. The leads may be buried in the surface of unpaved streets, or laid upon asphalt blocks or brick pavement, and a board nailed over them to protect them from traffic.

(*D*) **Terminal Connections for Over-All Potential Measurements.**—Methods of making connection of the lead wires to rails are of great importance, and careful attention to this detail will

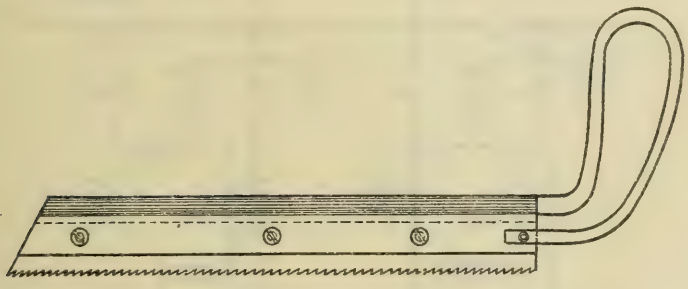

FIG. 2.—*Special hack saw for slotting rails and pipes for making swedged connections*

save much trouble from errors in readings or broken connections. Holding a wire on a bright spot on the rail is feasible, but is tiresome for the assistant, and the contact is rather uncertain at best. A file with a soldered lead may be held on the rail when a contact for a short time only is desired, but a much more certain contact is obtained by swedging a wire into a slot in the outside of the rail head where it is out of the way of cars. Such a connection (see Fig. 1) can be made so quickly and has been proven by experience to be so strong and durable that it is recommended even for temporary work. The usual hack-saw frame does not permit making a slot in such a small space, and a special saw frame made of steel, as shown in Fig. 2, is very convenient for this work and also in making connections to pipes, mentioned later under the discussion of current measurements. Magnets have been used, but experience has shown that the electrical connection is not as reliable as in the case of a swedged joint.

In order to make contacts on the ground or pipe systems it is preferable to use fire hydrants or gas or water service-pipe connections where these are available, but in case they are not available, several driven pipes connected in parallel will furnish a reasonably low-resistance ground with less danger from galvanic potentials than if one pipe is used. The metallic connections to water or gas mains furnish very low-resistance contacts, and the potential differences on these systems are more directly comparable with the danger of such systems than the measurement on the ground with small-area contacts. Where the potential differences in the ground are small it may be necessary to use nonpolarizable electrodes, such as described later, in order to obviate the galvanic electromotive forces.

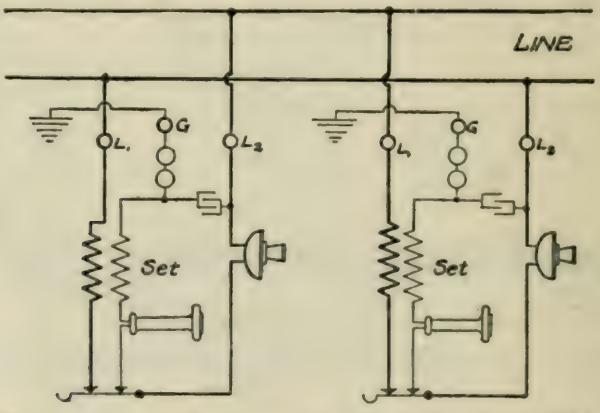

FIG. 3.—*Diagram of a common type of two-party circuit which can be used for securing temporary ground connections*

The contact in the ground or to the rail may be made before the test, and when using idle lines the lead to ground or rail can be permanently connected to the telephone wire so that a workman need not be sent to each point when making measurements, all connections being made in the telephone central stations. Such permanent connections should be made whenever possible, as they will greatly reduce the time and labor required in testing. Temporary grounds, such as single-driven ground rods, are undesirable because of the uncertain and high-contact resistance which is likely to exist. There are many good grounds on a telephone system which are tested for resistance and are required by company regulations to be below a certain value, frequently 70 ohms. These grounds are placed at terminal boxes and at certain types of telephone instruments—for example, prepayment telephones

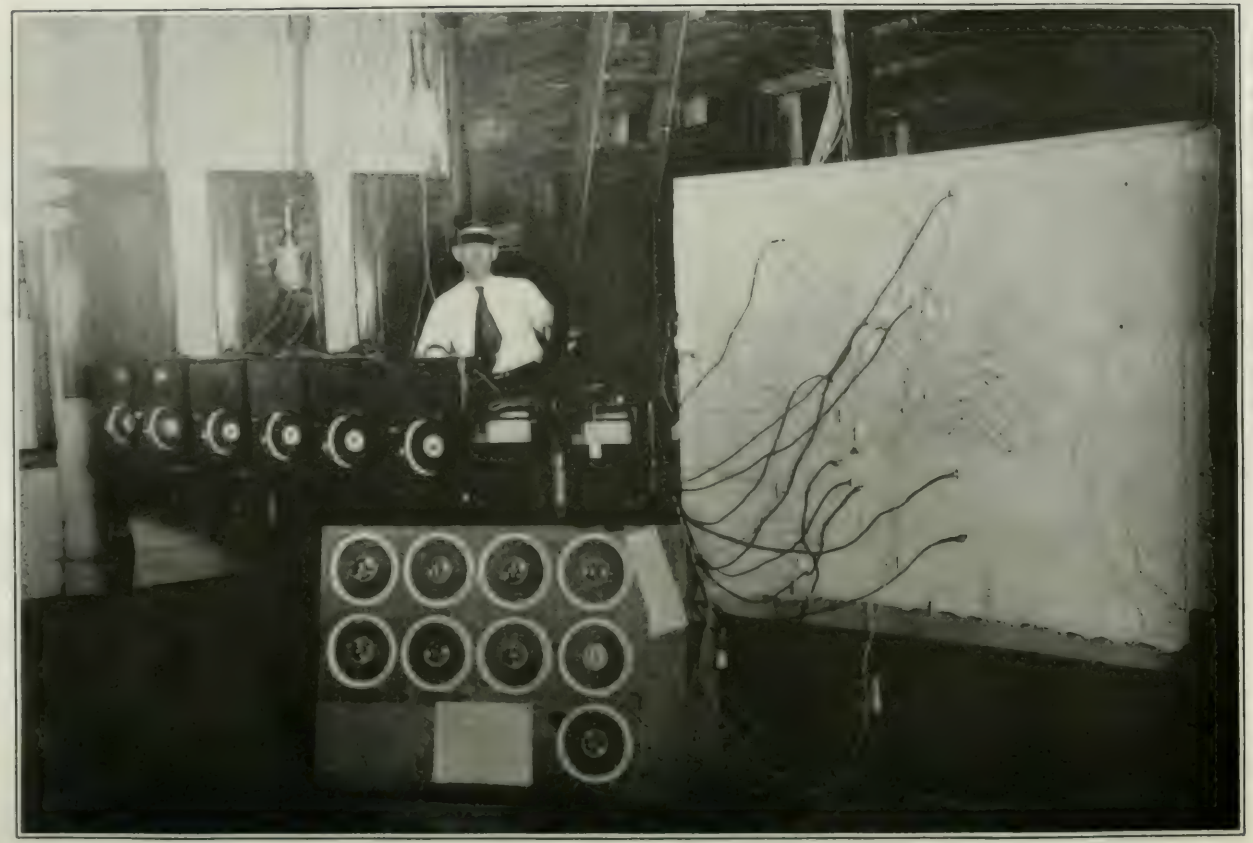

FIG. 4.—*Arrangement of connections for measuring over-all potentials*

and some party-line telephones. Fig. 3 shows the connections of one type of two-party circuit, and by tracing them it is seen that with the receiver off the hook a connection exists between the ground and both sides of the line through certain resistances.

(*E*) **Procedure in Making Over-All Potential Measurements.**—(*a*) PRELIMINARY PLANS.—In instituting an over-all potential survey in a city it is first necessary to determine the location of the points between which potentials are to be observed. As a rule, not only maximum potentials should be measured but leads should also be run, as described above, to a good many intermediate points to permit taking potential gradient measurements, as described later.

By consulting a railway positive feeder map a list of power stations and their extreme feeding points can be made. If a complete set of readings from remote feeding points is desired, special lines to these points may be run or leased from the telephone company. With the above list of points to be reached the telephone officials can prepare a table showing the terminal boxes, pair and cable numbers, including trunk cables, which are necessary to make complete circuits between one of the telephone central offices or other point where the measuring instruments are placed and the power house and feeding ends. A large city map mounted on a board, as shown in Fig. 4, showing railway lines and having binding posts with connections on the back to the terminal room and on the front for the instruments will expedite the work and insure greater certainty of correct connections, especially where measurements are to be repeated. The wire running from any point on the street is connected to the back of a binding post piercing the map at the corresponding point. After the correct connection of wires has been verified one can readily connect a voltmeter between the wires leading to any points in the city without danger of error.

Readings are first made between the negative points in each power-station area in order to determine the point of lowest potential in the city. Measurement can then be made from this low point to all other points selected and between any two points as desired.

(*b*) METHODS OF MAKING TEMPORARY CONNECTIONS.—Where for any reason permanent connections to tracks can not be made as explained above, temporary connections become necessary, and these require considerable time and expense for labor. For

instance, in case a temporary potential terminal on the rails is desired, a workman must go to the point, run a double wire from the two sides of the pair in a near-by terminal box, and make contact on the rail. With the common telephone the workman can report when ready and receive instructions over the same wires used in the potential test. If the terminal-box grounds are used a workman must go to each point and make such connection. A ground on a lead-cable sheath should be avoided as it may carry current from some distant point with a very different potential.

When a workman is not required at the point at the time of observation, as when telephone instrument grounds are used or other connections installed previous to the tests, the measurements may be taken efficiently and quickly. The ground at coin box or prepayment telephones may be made use of by placing a coin in the slot, thus completing the circuit between the ground and the line. Certain two-party lines, which have a ground at each instrument and where the selective ringing is done over opposite sides of the line and ground return circuit, may be used when the receiver is taken off the hook. It is necessary in any case to ring the telephone at the point desired and ask the party to place a coin in the slot or to leave the receiver off the hook for a short time.

(*c*) Avoidance and Correction of Errors.—When a series of readings has been obtained certain corrections may have to be applied. The most obvious is that for resistance of leads in series with the instrument. If the resistance of the instrument is high, the external resistance will be a small per cent of the total and since the value of the external resistance is sometimes uncertain, it is desirable to keep it as low as possible. The resistance in the telephone central stations is reduced to a very small value by avoiding running the circuits through the switchboard. The resistance of the lines may be definitely determined. It is common practice to use No. 19 copper in trunk cables, which has a resistance of 88 ohms per loop mile, or 44 ohms per wire per mile, or 22 ohms per mile paralleled. The other cables have No. 22 wire which has twice the resistance of the trunk pairs. If special lines are erected for the survey, they will be heavier to provide mechanical strength, and in this case the size and length will be definitely known. Since the leads will seldom exceed 10 miles in length, the resistance will not exceed 300 ohms or 1 per cent of a 30 000-ohm instrument. This is not a very important correction on observations of a potential which may vary from zero to 200

per cent of the average value, and can be neglected. Special indicating instruments having ranges of about 15 volts and a resistance of the order of 30 000 ohms can readily be obtained. When, however, an ordinary Model 1 Weston portable voltmeter of 15-volt range is used the resistance would be about 1500 ohms, in which case the error due to 10-mile leads would be about 20 per cent and would require correction. The resistance of the contact when connection is made direct to rail would, in practically all cases, be only a fraction of an ohm. The greatest resistance is found when a telephone instrument ground is used, since by referring to Fig. 3 it will be seen that in this case the bell coils (varying in the different types of telephones from 500 to 2500 ohms), one side of a mutual inductance and receiver are directly in series while an inductance and the transmitter parallel each other and are in series with the circuit. This requires that an appreciable correction be applied when ground connections are made through such circuits. When a recording instrument is used the external resistance will probably be a considerable percentage of the total resistance, since these instruments usually have a lower current sensibility and resistance than the best indicating instruments. Where pairs of wires are used the resistance can be measured by making a loop and the correction calculated or the instrument may be calibrated on each circuit, by means of a special indicating instrument of very high resistance. The latter is generally desirable as a check and is generally more accurate owing to the possibility of unknown resistances in the circuit.

In making connections in the telephone central stations, the switchboard equipment, plugs, jacks, etc., might be used and thereby expedite the work, but the resistance and uncertainty of sleeve contacts, coils, etc., and the possible introduction of the operating potential are sufficient reasons for avoiding the station circuits by connecting directly to the incoming and outgoing wires on the terminal frames. The accidental impression of the telephone operating potential must be guarded against, since it is very possible for this to occur and thus render all readings worthless. An examination of the circuits, or a careful examination of results, usually will reveal the presence of such an extraneous potential, if any exists. The telephone potential is usually as large or larger than most over-all potential drops and is practically steady, and for this reason can easily be distinguished from the railway voltage.

(*d*) GENERAL PROCEDURE.—While making over-all potential measurements, as well as in all other electrolysis tests described later in this paper, it is advisable wherever practicable to arrange to have the test data worked up and tabulated, and preferably laid out on maps as the work proceeds. In this way it is possible to keep in close touch with the progress of the work; and by making a study of the preliminary data before the work is finished it is often possible to modify the original plans in such a way as to obtain more complete and accurate data regarding electrolysis conditions. It has a further advantage in that it will bring to light any apparent inconsistencies in the readings at various points in time so that these can be checked and the uncertainties eliminated.

In over-all potential measurements, as well as all other electrical measurements made in connection with electrolysis surveys, it is desirable to take the readings at each point over as long a time as circumstances will permit. The variability of such readings, due to the fluctuating character of railway loads, is usually such that readings taken over a period of a few minutes only may give a very misleading impression as to the conditions which actually exist. This is particularly true where infrequent car schedules prevail. On a line on which the 15-minute schedule is maintained it will be found that certain of the readings, such, for example, as potential-difference measurements between pipes and rails, will vary periodically between wide limits, depending on the condition of the cars. Periods of several minutes may elapse during which the reading will be very small, and this will be succeeded by a short period of a few minutes' duration during which the readings may be several times greater. Obviously, it is important in such cases to continue readings throughout a complete load cycle. Care should be taken that the period is either substantially one-load cycle or an exact multiple of a load cycle. It will be apparent that if the reading is taken, say, over one and one-half load cycles, the reading may include either two hollows and one peak of the voltage curve or two peaks and one hollow, and in the latter case the average value will appear much larger than in the former case. Very large errors often result in this way, so that care should be taken to minimize such errors by determining the period of the load cycle before determining upon the length of time over which the reading is to be taken. Of course if the load cycle is short, so that the reading can be continued over a con-

siderable number of cycles, the error due to this cause will be negligible.

Wherever conditions will permit it is desirable to continue the readings at any point for a period of about one hour, and in the case of very infrequent schedule, as on certain interurban lines, even a longer period should be adopted. Even then it will be necessary, if accurate conclusions are to be reached, to reduce these readings to some equivalent average values for a longer period, such as a day or longer. This matter is discussed in some detail in a later section of this paper dealing with interpretation of electrolysis surveys.

2. POTENTIAL GRADIENT MEASUREMENTS

(*A*) **Definition of Term.**—A potential gradient is the rate of change of potential along a conductor. It is generally expressed in volts per thousand feet, but this is intended to convey the idea of the rate per thousand feet at any point and not that 1000 feet is the exact length to be employed. Under the head of potential gradients will be included all potential measurements between two points on the tracks or between two points in the earth over distances materially less than the extremes of the power-house feeding area. In using the term "gradient" it must be borne in mind that the rate of change of voltage may not be regular, as, for example, if high-resistance joints or other irregularities in resistance of the circuit are encountered.

(*B*) **Measurement of Potential Gradients in Tracks.**—Potential gradient measurements are usually made in the railway tracks but sometimes also on the pipe systems in the earth. The same method of making contact with rails, the same types but slightly lower ranges of instruments, and often the same kind of leads as those described under over-all potential measurements may be used in obtaining potential gradients in the rails. The procedure will often be different, however, because the distances are generally shorter and may be spanned in a more convenient or economical manner than by the use of telephone wires. The points to be reached must be selected and a decision made as to the type of leads best suited to reach these locations. If spans are quite long, such as several thousand feet, telephone or pilot wires may be used, as in over-all potential tests, and in that case there would be no difference in procedure from that described above for making over-all potential measurements. If the dis-

tances over which the over-all potential measurements are to be made are two or three thousand feet or greater, it will be much better to use telephone lines. When, however, it is desired to measure gradients between many points a thousand feet or less apart it will generally be easier to run a short span of wire directly between the points between which the gradient is to be measured, as described later.

The apparatus necessary in making rail gradient measurements includes voltmeters, leads, and suitable contact terminals. Since the gradient often ranges from a fraction of 1 volt to 20 volts or more per 1000 feet multiple range instruments are necessary. Instruments giving ranges from 1 to 50 volts are not unlikely to be required. It is practicable to secure instruments of suitable ranges so that they can be used in both the over-all potential and potential-gradient measurements as well as for many other tests. Such instruments are described later in this report. The telephone lines used as leads and the rail contacts have already been discussed, but in measurements of shorter spans of 1000 feet or less a length of wire on a special reel and equipped with a crank and brake will expedite the work. The wire can be paid out from the reel along the side of the street and raised above crossings where traffic would cut the wires or insulation. The kind of wire is important, the most suitable being flexible No. 12 or 14 gauge copper wire with good rubber insulation impregnated to resist moisture. Solid wire is so easily broken by traffic or in handling that it should not be used, and a flexible wire is recommended. For measurements made in this way portability and ruggedness in the voltmeters are more important than when the measurements are made at some central point with the aid of telephone wires.

The contact terminals used will depend on whether the measurement is to be made between the points on a track or pipe system or between the points in the earth. For making measurements between points on the tracks or on a pipe system or other metallic structure any metallic terminals held firmly against the rail or pipe, or a wire swedged in the slot after the manner described above under over-all potential measurements may be used.

(*C*) **Measurement of Potential Gradients in the Earth.**—(*a*) Need of Making Earth-Gradient Measurements.—Measurements of potential gradients in the earth are useful in showing the general conditions in a railway feeding area, but more especially in

determining local conditions. The desirability of a general earth survey may be questioned, since the potential gradients on the rails or on pipe systems are such excellent indications of conditions and are much more easily obtained and more accurately measured. However, special situations may arise where potential measurements between various points in the earth are necessary, and they are useful for many purposes. The presence and direction and approximate magnitude of large transverse currents which enter one side of the intercepting main and produce damage upon leaving may thus be revealed. High-resistance joints of an underground main may be located more rapidly by gradient measurements in the earth above the pipe than by excavations. A formerly common street-railway practice of placing large ground plates as distributors or collectors of the return current in moist earth has not been entirely abandoned. This is objectionable, although its continuance in some cases may be unintentional. Gradients radiating from such terminals may be traced by a series of earth-gradient measurements. The gradients are greater close to the electrode, and thus the existence and location of such grounds can be determined. Buried pipe lines or other conductors of uncertain locations which are discharging current into the earth may be located by gradient measurements, there being usually a reversal or abrupt change in the gradient when the buried conductor is crossed.

(*b*) Instruments for Earth-Gradient Measurements.—The procedure, and especially the equipment for earth-gradient measurements, differs from those used for measuring rail gradients. Three sources of error are encountered in these measurements which are not met with in rail-gradient measurements, namely, electrode potential drop, galvanic potential differences at the electrodes, and polarization potentials. Since the values of the gradients are often small, a comparatively long span and an instrument of high sensitivity is necessary. In a number of surveys made by the Bureau of Standards a span of 500 feet was used and gradients great enough to overshadow small galvanic potential differences were obtained. The range of the voltmeter used should extend from a few millivolts to about 10 volts for most purposes. In order to eliminate errors due to the resistance in the earth near the contact terminals it is generally necessary to use an instrument of very high current and volt sensitivity, so that a high resistance can be connected in series with the instru-

ment sufficient to make the resistance of the earth contacts practically negligible. An instrument having a resistance of from 2500 to 3000 ohms per volt requiring from 0.4 to 0.3 of a milliampere for full-scale deflection is desirable for this work. A portable voltmeter of this kind can be readily obtained from instrument manufacturers. A portable galvanometer having a current sensitivity of 0.5 microampere per centimeter and having a high resistance in series has been used very satisfactorily for this and for other measurements mentioned later. This instrument is made by Leeds & Northrup Co., does not require extreme care in handling, and has proven very rugged in use. It has been mounted on a surveyor's tripod, which makes a very convenient arrangement for leveling and making observations. The use of a potentiometer for this work is not recommended, since this equipment is heavy and delicate and requires a zero setting, and hence is not well suited for field work where rapidly varying voltages are usually encountered.

(*c*) Leads and Terminals for Earth-Gradient Measurements.—The leads used in making earth-gradient measurements should be thoroughly insulated throughout their length. The contacts or electrodes are the most vital part of the equipment and special attention must be given to these in order to eliminate errors due to galvanic action and polarization. If iron rods are driven into ordinary soil, galvanic potential differences of from 0.01 to 0.1 volt will often be indicated, while the same rods in soil mixed with coke or cinders or affected by local surface seepage from city streets will produce voltages of half a volt or more. To eliminate these galvanic potentials, nonpolarizable electrodes have been devised and described by a number of investigators. One type which the Bureau of Standards has found most satisfactory is shown in Fig. 5. It consists of an electrode of copper immersed in a copper-sulphate solution contained in a cement cup. Another type consists of an iron tube containing a solution of ferric chloride, the lower end of the tube being closed with a porous substance such as a compressed sponge. The outside of the tube should be insulated so that electrical contact with the earth is made only through the moist sponge. The resistance between this copper-sulphate terminal and ground will seldom exceed 250 ohms except in exceedingly dry soils, and in such cases a little water poured into the holes around the electrode will suffice to reduce this resistance to a point where it will not materially affect the reading of a high-sensitivity portable voltmeter.

When two electrodes of this kind are used troubles from polarization at the electrodes are eliminated. These terminals are used by driving an opening in the earth with a bar and filling this with water to a level sufficient to cover the electrode and inserting the latter. The lead wires are then connected to the voltmeter or other indicating instrument used, and the reading taken.

Where it is desired to take a potential reading between a lead cable sheath or an iron pipe and a point in the earth, such an elec-

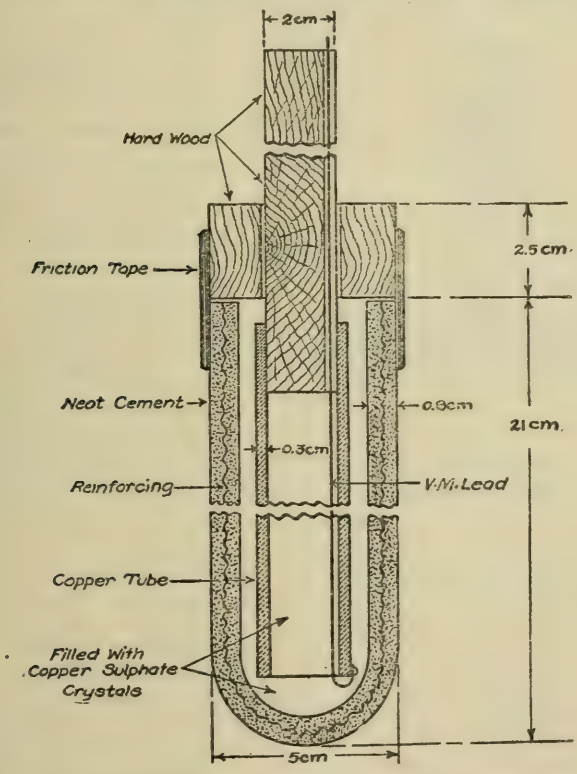

FIG. 5.—*Nonpolarizable electrode suitable for making contacts with earth*

trode should not be used for the earth terminal, since a battery effect would be obtained due to the dissimilar character of the electrodes. If the potential difference is to be taken between lead cables and the earth, a lead electrode should be used. Potential-difference measurements between iron pipes and a point in the earth are likely to be unreliable because of the presence of more or less iron oxide on the surface of the pipes which may affect the polarization potential. Where it is desired to measure a potential gradient in a direction at right angles to the pipe and

close to the same, it is better to use two nonpolarizable electrodes, one very close to the pipe and the other a little farther away. If the potential is high enough to be at all serious, it will be practicable to measure the potential drop over a foot or so in length which would answer the purpose very well.

(*D*) **Measurement of Potential Gradients in Concrete.**—It has been shown by numerous laboratory experiments that under certain conditions flow of electric current through reinforced concrete will produce certain deleterious effects at the electrodes. These effects, although quite uncommon in practice, need to be guarded against under certain unfavorable conditions, and it sometimes becomes necessary to make measurements of potential gradients in different parts of a concrete structure. To do this it is best wherever practicable to make measurements between different parts of the reinforcing material or other embedded metal in the concrete, where these are not metallically connected together. Where such terminals are not available, however, it may be necessary to measure potential differences between two points in the plain concrete. In this case, as in the soil, an electrolyte serves as a conductor in the concrete, and the same sources of error are encountered as in making potential-gradient measurements in the earth. In particular, the resistance in the concrete near the electrodes will often be much greater, especially where the concrete is above grade, and hence fairly dry. Since openings in the concrete are not easily made and the length over which measurements are taken is short, different contacts and a greater sensitivity in the instrument are necessary. Only a portable galvanometer can be used for this work. A suitable contact, shown in Fig. 6, consists of a copper cup with a piston which forces the

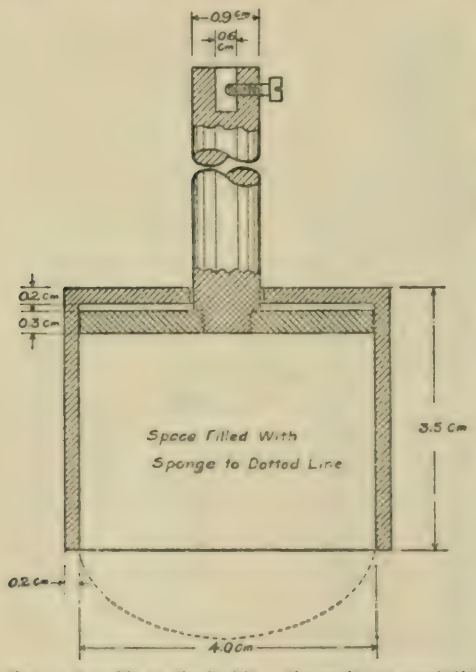

FIG. 6.—*Nonpolarizable electrode especially adapted for making contact with walls of concrete structures*

sponge saturated with copper-sulphate solution against the concrete surface. The contact resistance varies with the moisture content in the concrete and with a sensitive portable galvanometer, such as described under earth-gradient measurements. The resistance of the circuit can be of the order of several hundred thousand ohms, so that the resistance of the concrete near the contacts will be negligible in practically all cases. When testing between ordinary reinforcing material and a point in the concrete, an iron electrode in a solution of calcium hydroxide should be used. It can be made up in the same form as the copper electrode described above.

3. MEASUREMENTS OF POTENTIAL DIFFERENCES BETWEEN PIPES, RAILS, AND OTHER CONDUCTORS

(*A*) **Definition of Term.**—The term "potential difference" is here used in reference to voltage measurements between various systems of conductors. For example, between pipes and rails, lead sheaths and rails, lead sheaths and ground, and a number of other combinations. The distinction made between gradients and potential differences is that gradients are values obtained between two points on a single conductor, while potential differences are measured between two different conductors.

(*B*) **Purpose of Potential-Difference Measurements.**—Potential-difference measurements are probably the measurements most commonly made in electrolysis surveys and are justly given great importance, for when interpreted with due consideration to other circumstances they afford a valuable index to local electrolysis conditions. Some ordinances specify the maximum potential differences which will be permitted. However, a low potential difference does not always indicate a safe condition, nor does a high potential difference necessarily indicate a condition of danger. The possibility of a low or high resistance path must be considered in interpreting such data. Nevertheless, a considerable number of potential-difference measurements should be made in electrolysis surveys, since when properly interpreted they assist materially in determining electrolysis conditions.

(*C*) **Number and Location of Measurements.**—Potential-difference measurements should be made at selected points between fire hydrants and tracks, lead cable sheaths and tracks, lead cables, and any accessible pipe systems, and in many cases between different pipe systems occupying the same territory. These measurements should be made throughout a large part of the

railway feeding area, including many points in the neutral and negative areas as well as in the regions where the buried metal structures are, in general, positive to the railway tracks. This is necessary because there are many places where certain or all of the pipe and cable systems may be negative to railway tracks, but some of them may be more strongly negative than others, and consequently set up a condition of danger to the latter. This is particularly apt to be true where excessive pipe drainage is used for the purpose of reducing the potential differences in the positive areas.

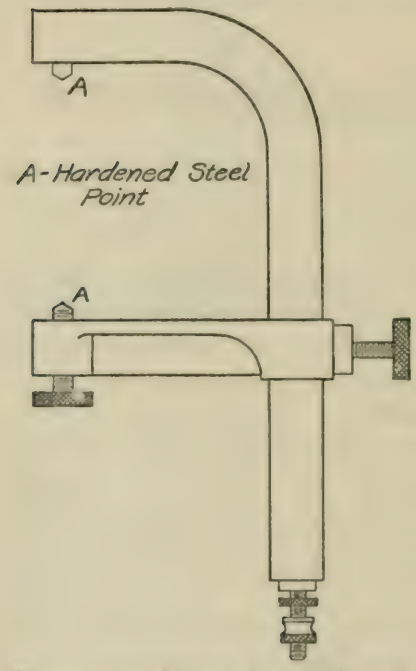

FIG. 7.—*Special clamp for attaching voltmeter leads*

(*D*) **Equipment for Potential-Difference Measurements.**—In case potential-difference measurements are to be taken between metallic conductors the current sensitivity of the voltmeter is not important, since spans or leads are usually short. The ranges necessary do not differ greatly from those required for over-all potential measurements, although the readings are, in general, somewhat lower and the same instruments are practically always used. In the potential-difference measurements, however, a zero-center instrument is very desirable, since a large proportion of these measurements will show frequent reversals.

Since the objects between which potential-difference measurements are made are usually close together, short leads are usually all that are required, and for contact the wire swedged in a sawed slot, as described above, under over-all potential measurements may be used. Use may also be made of a "C" clamp, or better, a special clamp after the design shown in Fig. 7. The clamp has a large spread of jaw, hardened points, and a place for attaching wire. In cases where the contact point is to be held in during measurement it should have a good insulating handle designed to prevent the hand getting in contact with the metal during meas-

urement, as the values may often be so low that an extraneous potential of small proportion might invalidate the reading. When measuring potential differences between points in the soil the nonpolarizable electrodes, such as described under potential gradient measurements, must be used in the electrolytic conductors.

II. CURRENT MEASUREMENTS

1. DEFINITION AND IMPORTANCE OF CURRENT MEASUREMENTS

Under the head of current measurements are included all observations of current flow obtained by ammeter readings or by a potential drop on a conductor, the resistance of which is approximately known. They include also measurements of the leakage of current from pipes or cables into the earth. The amount of current carried by underground structures is often so closely related to the total extent of the damage produced that a knowledge of its magnitude is often very desirable. There are a variety of conductors in which it is at times necessary to measure the current, including copper feeders, railway rails, cast-iron, wrought-iron, steel, and lead pipe, lead cable sheaths, reinforced concrete structures, and occasionally in portions of the soil.

2. MEASUREMENT OF CURRENT IN FEEDERS AND RAILS

(*A*) **Need for Measuring Current in Feeders and Rails.**—Measurement of current in feeders and rails is not necessary where it is desired merely to determine the degree of danger which exists to underground structures. When, however, it is desired to design a system of mitigation with a view of reducing the leakage of stray currents into the underground structures, it is necessary to secure complete data regarding the magnitude and distribution of the railway loads, not only in positive feeders, but in the negative feeders and tracks also. Measurement of current in tracks is also useful because such measurements when properly made and interpreted often give a good idea as to the proportion of the total railway load that is leaking off into the earth. They also show at what points return feeders should be connected to the tracks in order to take off the current without permitting unduly large voltage drops in the track return. They further show the approximate amount of current that needs to be taken off at each point, and hence the size of the feeder that would be required. Such measurements are often of value also in esti-

mating the losses in the negative return; and by measuring currents in different rails of a track, local bad bonding will be revealed by unequal distribution of currents between the different rails of the track. In fact, the quickest and most reliable way to get a good idea of the general condition of the track bonding is to test for equality of distribution of current in the rails at numerous points.

(*B*) **Methods of Measurement.**—(*a*) DIRECT MEASUREMENT WITH AMMETER OR SHUNT.—An ammeter or shunt inserted in the feeder or rail circuit is the most accurate method of obtaining current measurements, but it is often the case that feeders, particularly negative feeders, are not provided with ammeters, and it is usually difficult and often impracticable to insert them. In such cases a potential-drop measurement on a portion of the cable or rail, together with data concerning the cross-section and resistivity of the conductor, form the basis of a much more convenient and sufficiently accurate method of measuring. An instrument well suited for current measurements in all metallic conductors is an indicating or recording millivoltmeter of 10, 100, or 1,000 millivolt range. The lower ranges of the recorder described elsewhere in this paper for other purposes are well adapted for this work. A high current sensitivity is not essential, since we have here a low-resistance circuit and good contacts with no galvanic effects. Suitable terminals for connecting the instrument leads to rail are shown in the accompanying illustrations. Fig. 8 shows a contact point *a* with a long handle *b*, and flexible cord *c*, the slack of which can be taken up in the hooks *d*. Fig. 9 shows a rail spanner that has proven very convenient for measuring current in rails with indicating instruments. The spanner is a frame carrying two hardened points or portions of hack-saw blades at a fixed distance apart, preferably about 4 feet, and insulated from each other. A handle is provided for convenient application to rails on which it is designed to be used. It is made of aluminum, thin brass, and wood, is very light, and is made with a screwed handle so that it can be taken down and packed in a small space. This rail spanner has been found light and convenient enough so that one observer can handle it and an indicating voltmeter and get rapid and accurate results. Where a recorder is to be used for taking measurements during a period of considerable length, swedge connections to the rail, like those described above under over-all potential measurements, should be

used. The data concerning the resistance of the conductor can be obtained by an electrical calibration at each point or by a calculation from the cross section and specific resistance of such conductors. The latter is much more convenient, and is accurate enough for most practical purposes, and is quite generally used. Where high accuracy is sought, however, a calibration is necessary, and various methods for making a calibration are described below.

(*b*) Calculation of Current from Voltage Readings.—In the case of copper cables the cross section and specific resistance

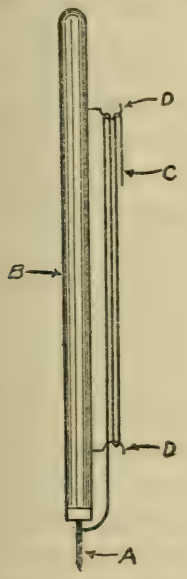

Fig. 8.—*Contact point with insulating handle*

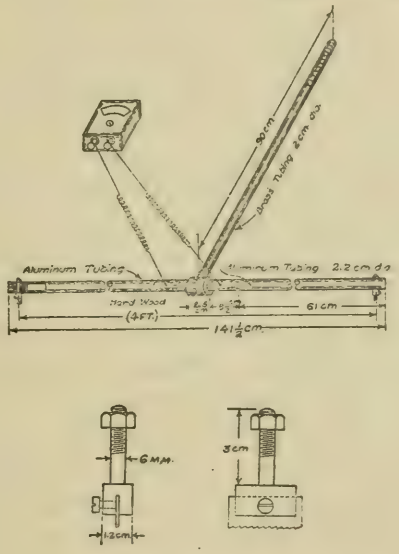

Fig. 9.—*Rail spanner for making contacts on a short length of rail*

are known so accurately that a calculation based on this data is sufficient for all purposes of electrolysis surveys. For example, taking the resistivity of copper at 10.7 ohms per mil-foot, if a 1 000 000 circular mil-cable has a drop of 6 millivolts on a 5-foot length the current will be given by the equation

$$I = \frac{E}{R} = \frac{0.006}{5} \times \frac{1\,000\,000}{10.7} = 112 \text{ amperes.}$$

This value would generally be correct within a few per cent, since all the values entering into the calculation are known or can be measured with an accuracy of at least 1 per cent. If the cable carries sufficient load to make it perceptibly hot and a high

accuracy is desired, an allowance must be made for temperature coefficient of copper. When rails are the conductors, neither the cross section nor the resistivity are so accurately known as in the case of copper, since rails vary widely in weight, composition, and heat treatment. The composition and heat treatment of steels affect resistivity so decidedly that variations of from 9 to 20 microhms per centimeter cube occur. Modern practice is tending toward greater uniformity of carbon and manganese content, and also toward harder steel with higher resistivity. It is desired, where convenient, that the conductivity of sample sections of the rail be determined for each particular installation in case high accuracy is desired. In lieu of this a very close estimate can be arrived at from the composition or the exact conductivity for the product as given by the manufacturer. Tests made by the Bureau of Standards on a number of rails show considerable variation in both resistance and weight. One specimen of T rail having A. S. C. E. section rated at 80 pounds per yard was actually 15 per cent lighter than this weight, and its resistance was 0.0002975 ohm per pound-foot. Two specimens of rail, one 95-pound tram rail and one 112-pound trilby, had resistivities of 0.00028 and 0.000315 ohm per pound-foot, respectively, giving the same average as the first and a maximum variation of 9 per cent. Resistivities varying between 0.000275 and 0.00035 ohm per pound-foot have been encountered in rails in service, but these represent rather extreme and unusual variations. If the value of 0.0003 ohm per pound-foot (which corresponds to over eleven times the resistivity of copper) is used, the results can in most cases be depended upon to within 10 per cent, which is usually close enough when we consider the highly variable character of the terms to be measured. As an example of a method of calculation, using the values of the various quantities in terms of the units commonly obtained in observation, we take the following example. If the potential drop in the rail is E volts per yard, and the weight of the rail W pounds per yard, the current in the rail I, in amperes, will be given by the equation:

$$I = \frac{EW}{0.0003 \times 3}$$

3. MEASUREMENT OF CURRENTS IN PIPES AND CABLE SHEATHS

(*A*) **Purpose of Measurements.**—The measurement of current flow in pipes and lead cable sheaths and other buried structures is important for a number of reasons. Large currents in the

pipes are accompanied by the danger of corrosion on the positive side of high-resistance joints which may occur at many points throughout the pipe network, particularly in cast-iron mains. Also heavy currents set up high potential gradients in the pipes and thereby tend to produce large potential differences between neighboring pipe systems, causing the one of higher potential to discharge current into the one of lower potential, resulting in injury to the former. Further, when heavy currents are flowing in pipes there arises a danger from arcing at points where the pipe line and its connection are opened for any reason. This danger is particularly great in the case of gas pipes where an arc might ignite escaping gas. There is also a danger of arcing where two pipes of different potential make momentary mechanical contact. Cases have also been brought to our attention in which lead cable sheaths had been overheated, and even water service pipes and their connections had been heated to a red heat.

In order to guard against these and other dangers it is important to keep the current flow in pipes at as low a value as practicable, and hence the importance of making current measurements in buried pipes in many instances. Furthermore, the relative magnitude of the current flow in pipe systems at given points both before and after the installation of electrolysis mitigation measures offers a valuable index to the effectiveness of the measures adopted. Such measurements are also useful in many cases in determining the source of stray current. A recording meter measuring the current flow in a pipe at the same time that a measurement is being made of the railway load supplying the district from which the pipe collects its current will often afford, through a similarity of the records, definite evidence regarding the sources of the stray current. Such measurements are particularly useful where two or more railway lines operate in the same vicinity.

(*B*) **Selection of Points of Measurements.**—It is very important in making current measurements in pipes to select carefully the points at which the measurements are to be made. Points of representative and of maximum current flow are usually desired in making such observations, and since tests are rather expensive, requiring excavations in the case of pipes, careful selection of locations is necessary. In the case of a street railway line paralleled by a pipe line the maximum current will occur at the point where the pipe is neutral to the rails, but this ideally simple condition does not exist in city networks, and the greater concentra-

tion of current usually occurs within the positive area. Current measurements should usually be made in mains which extend in the general direction of the potential gradients in the earth. These are, in general, toward the supply station and can be readily determined in any particular case. By consulting a map of the pipe networks, including both gas and water systems, the pipes most likely to be carrying current are usually quite evident. Mains running more or less at right angles to the direction of current flow in the earth serve as equalizing busses, which distribute the current among the radiating mains leading into the power-house area. This distribution, however, is disturbed by high-resistance joints, especially in cast-iron mains, and the selection of the particular main or set of mains carrying the maximum current is usually difficult. Where only a few mains extend in a direction away from the power house, measurements of current can readily be made in all of them. Otherwise, a representative number should be chosen for current measurements from which an estimate of the total current sufficient for most purposes can usually be had. In any event the exact value of the total current flow is not so important as the order of magnitude of the current, the source whence it comes, and the secondary effects on other underground systems to which it may give rise.

(C) **Methods of Measuring Current Flow in Pipes.**—Three general classes of methods of measuring current flow in pipes and other metallic structures have been used. The first of these, and the one used in the great majority of cases, is the ordinary drop of potential method, in which the millivolt drop on a measured length of pipe is taken and the current calculated from the millivolt drop and the resistance of that portion of the pipe over which the potential drop was measured. Complete tables giving the resistance per unit length and much other data regarding all of the common sizes and kinds of pipe used in practice are given in Table 1 below.

The second class of methods comprises all those in which an auxiliary or derived circuit is used to shunt out all or any portion of the current in a section of the pipe on which the millivolt drop is being measured, the current being shunted out being measured by an ammeter, and its percentage of the total determined from the percentage drop in the millivoltmeter reading on the section from which the current is shunted. These methods have taken various forms and are described later under the head of "Divided

circuit methods." In most cases a battery is used in this auxiliary circuit. The third method consists in the use of what is known as a direct-current ratio relay in a manner somewhat analagous to the use of a current transformer in alternating-current instruments.

These last two methods are chiefly useful for calibrating a section of pipe in order to eliminate in some measure the uncertainties arising from the use of the tables. They are desirable, however, only in cases where high accuracy is sought, such, for example, as when securing evidence to be presented in court, or where it is desired to measure the leakage of currents from a given section of pipe by an accurate measurement of the current at two points, the difference between which measurements would give the values sought. In such cases extreme accuracy is necessary, and it is not safe to assume a value for the resistance of the pipe. These different methods of measuring current flow in pipes are described in detail below.

(*a*) Drop of Potential Method.—This method, which as stated above consists merely in connecting potential terminals to a section of pipe a few feet apart and measuring the millivolt drop and calculating the current from the voltage drop and the resistance of the section as determined from the accompanying tables, is very widely used, and it is accurate enough for most purposes. Its great simplicity especially adapts it to work of this kind. The accuracy of the method depends chiefly on the character of the current flow and the knowledge of the resistance of the pipe. It will appear from the data presented below in connection with the pipe tables that the resistance of the pipe can practically always be depended upon to be within 10 per cent of the value given in the table and usually much closer than this. Further, the currents usually found on underground pipes fluctuate between very wide limits, so that when readings are taken with an indicating instrument it is usually quite impossible to determine the average value of the readings with an accuracy as good as 10 per cent. Even with a recording instrument an accuracy of 10 per cent is often quite difficult to obtain, particularly where a 24-hour record on an ordinary circular chart is used. It is evident, therefore, that it is hardly worth while in most cases to use a more complicated method in order to eliminate the possible error due to the assumed resistance of the pipe when errors from other sources are likely to be much larger.

38592°—16——3

The data on pipes and cable sheaths obtained in the study of this method of measurement are summarized in two sets of tables. In the first set of tables are shown the dimensions and weights of the various kinds and classes of pipe and lead sheaths. This set of tables is not needed in ordinary electrolysis survey work for obtaining values of current in pipe, but is given here for the purpose of showing the degree of variation to be expected in practice in pipes from different manufacturers, and hence the probable accuracy of the results obtained by the drop of potential method. The working tables to which reference must be made for reducing the millivolt reading to amperes constitute the second set of tables. These tables are derived in part from the first set of tables and contain the card size of the pipe, the weight in pounds per foot, the resistance in microhms per foot of length, and the current corresponding to 1 millivolt drop on 1 foot of length. In Table 1, showing the variations of the dimensions and properties of pipe from different manufacturers, the first column gives the laboratory number, the second column the card diameter, the third column the card weight in pounds per foot, the fourth column the observed weight, and the fifth column the per cent variation from the card weight. Then follow in order the specific gravity, measured resistance per foot of length, resistance per pound-foot, resistance per centimeter cube, and finally the percentage variation of each individual measured resistance from the mean of all the values in this section of the table.

Wrought-iron Pipes—In Table 1, section A, on wrought-iron pipe, will be found test data on 86 test specimens from different manufacturers, all the pipe being of standard weight, with diameters ranging from ¼ inch to 6 inches. The last 32 specimens are the product of one manufacturer and are included in this table because they are sold as wrought-iron pipe, although the resistance measurements indicate a higher resistivity than that of the steel pipe tested. Considering all of the pipes in this section of the table, the variations in weight per foot from the card weight show the pipe to be as frequently over as under weight, the average variation being 2.5 per cent. It will be noted that this variation is much greater in the case of the small pipes of one-half inch or less diameter. The average specific gravity of these specimens was 7.59.

In the resistance data it will be noted that the last 32 specimens referred to above have a resistivity of 14.39 ohms per centimeter

cube as compared with 12.78 and 12.97 for the two other groups; that is, it is higher than the steel, which was found to average 13.56 ohms per centimeter cube. This, of course, greatly increases the variation from the average, and this variation has an average of 4.77 per cent from the mean of the entire set. The average resistance of the entire set per pound-foot is 209.3 microhms.

Steel Pipe—There are 64 specimens of steel pipe from two manufacturers, the data on which are shown in section B of Table 1. Ten of these are boiler tube, on which no per cent of card weight is made, but since practically the same material is used in manufacturing as in the other pipe, the resistance of all specimens are included in the average. The weight variations are somewhat less than in the preceding table, even the small sizes checking very closely, and the average variation from the mean is 2.3 per cent. The resistance is 215.8 microhms per pound-foot and 13.56 microhms per centimeter cube, the value for copper being 1.59 ohms per centimeter cube, and the average variation from the mean is 2.3 per cent, the greatest single difference being 5.2 per cent.

Cast-Iron Pipe.—In section C of Table 1 are given data on 22 specimens of class B cast-iron pipe from two different manufacturers. The diameters range from 3 to 6 inches. The cast-iron pipe industry is quite different from the wrought-iron or steel industry, there being many small companies in the field and the uniformity of the product would not be expected to be as great as in the case of iron or steel pipe. It will be seen from the table that the average resistance per pound-foot is 1227 microhms and the resistance per centimeter cube 84.8 microhms. From these averages certain individual specimens vary as much as from 16 per cent low to 22 per cent high, and the arithmetical average of all the variations from the mean is 9.4. It was observed that internal diameter and wall thickness of these cast-iron pipes were on the average greater than the card values. The card weight shown in Table 1 is not that listed in the standard cast-iron pipe tables, because that weight includes the bell. In these tables the weight per foot is based on the card dimensions and the unit weight 0.264 pound per cubic inch, which figure is used by the manufacturers.

American Ingot Iron.—Thirteen specimens of American ingot iron pipe were received and the data are shown in section D of Table 1. No comparison of weights is made, since the dimensions

were not standard. The average resistance of 177.3 microhms per pound-foot, or 11 microhms per centimeter cube, indicates a much purer grade of metal than the wrought iron or steel discussed above.

Lead Pipe.—In section F of Table 1 are shown measurements on 27 specimens of lead pipe from one manufacturer, the sizes ranging from ¼ inch to 2 inches. A class was not specified in the specimens received, so they were rated in the class to which their weights most nearly corresponded. This would perhaps tend to reduce somewhat the variation in the results, especially since there are eight classes within the range, from very heavy to very light pipe. But lead works very easily, and is so homogeneous that a good uniformity of product might be expected, and an average variation from the mean of 3.9 per cent and an extreme of 10.2 per cent are probably as great as would usually be found in practice. It will be seen that in most cases the specimens were lighter than the card weight. The resistance data show the very decided homogeneity of commercial lead, the average resistance being 419.5 ohms per pound-foot and 21.12 per centimeter cube, and the average variation from the mean is only 0.5 per cent, while the maximum variations are between +2.1 and −1.4 per cent. The average value here given is about 10 per cent greater than generally given for commercial lead, but chemical analysis did not reveal any appreciable amounts of tin or antimony.

Lead Cable Sheaths.—Only a few specimens of lead cable sheaths, and these from one manufacturer, were tested. The practice as to size and thickness and chemical composition varies so much from time to time that any figures that might be obtained would be of little value, except where the composition is definitely known. The figures given in section G of Table 1 were those supplied by the manufacturer.

Copper Steel.—Several grades of copper steel pipe were tested and the results are shown in section E of Table 1. In this table the last column gives the kind of steel and the percentage of copper for the different grades. The specimens tested of a given grade were all uniform but there is considerable variation between the different grades.

In Table 2 there is summarized the resistance of the pipe in ohms per foot for the various sizes and kinds and also the number of amperes corresponding to a drop of 1 millivolt per foot, so that the voltmeter reading needs to be multiplied only by a constant

factor for any given kind and size of pipe. In the use of this table it is necessary to take the millivolt drop E on a portion of the pipe of length L in feet and then refer to the last column under the particular kind and class of pipe used and multiply the figure there found by the ratio of the observed voltage to the length in feet. For example, supposing we are measuring the current flow in a 10-inch cast-iron pipe of class B. Referring to Table 2 it will be seen that for this class a current corresponding to 1 millivolt drop on 1 foot is 42.4 amperes. If we are measuring over a length of, say, 8 feet and the observed millivolt drop is 3 millivolts, the current flow in the pipe will be $I = 42.4 \times \frac{3}{8} = 15.9$ amperes.

In using this method it is necessary first to make an excavation at the point where the measurements are to be taken and attach two leads to the pipe, preferably as far apart as practicable without including a joint in the pipe. These connections can be made in any one of a variety of ways, such as by drilling a hole in the pipe and screwing in a plug to which a lead has been soldered. This is all right for a thick-walled pipe, especially cast iron. For thin-walled pipe, however, it has been the practice of the Bureau of Standards to use the swedged connection such as described previously for making connections to rails in over-all potential measurements. If it is desired to use these connections for future measurements, the leads should be brought underground to a point inside the curb and there terminated in an ordinary service box or other suitable receptacle so that they will be protected from traffic but be readily accessible for repeating the measurements at any future time. If it is desired to use these leads for making measurements over a period of several months or longer, it is important to protect the junctions between the wires and the pipes from corrosion by painting them over with a heavy asphalt paint or other suitable protecting agency. The observation of potential can best be made with a millivoltmeter of high-volt sensitivity. A zero center instrument having a range of 10 millivolts on either side of the zero is usually sufficient where the current density in the pipes is relatively high. In many cases, however, where the current is small and the pipe relatively large, and especially in the case of wrought-iron or steel mains in which the resistivity of the pipe is low, a higher sensitivity instrument is often necessary. In such cases a portable galvanometer may be used. Where the currents are large enough to give a reading of 1 millivolt or more over the section spanned by the potential terminals an ordinary recording instrument can be used.

(*b*) DIVIDED-CIRCUIT METHODS.—Divided-circuit methods in various forms have been used by a number of investigators for many years. Probably the first to use them was Prof. Adams, of Columbus, more than 15 years ago, and it has been used by a number of other investigators. Credit for having first published a detailed description of the applications of various forms of this method and the procedure for the measurement of current in pipes by them is due to Carl Hering, whose paper was published in the Transactions of the American Institute of Electrical Engineers for June, 1912. The following description of the principle of the method is taken from Hering's paper:

The fundamental principle is as follows: Let *P*, Fig. 10, be a part of an underground pipe which has been uncovered and through which an unknown current *I* is flowing as shown. At first let it be supposed that this current is steady, and of course a direct current. Let *D* be a sensitive galvanometer, millivoltmeter, or any other form of detector of small difference of potential, connected as shown; there should

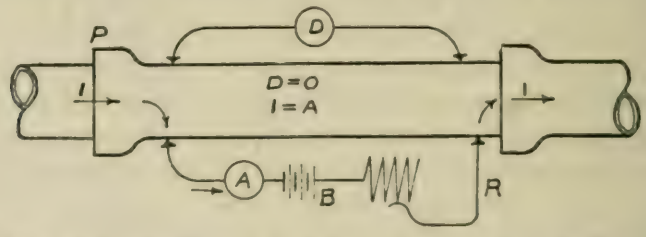

FIG. 10.—*Arrangement of connections for Hering's method of calibrating pipe sections*

preferably be no variable resistance like an unbonded pipe joint between the two contact points. Let *A* be an ammeter, *B* a few cells of accumulators, and *R* an adjustable resistance; the shunt circuit containing them is connected, as shown, anywhere outside of the points of application of the voltage detector, the farther away the better—they may even be on the other side of a joint.

To find the current flowing in the pipe adjust the resistance *R* until *D* reads zero; then there will no longer be any current flowing in the shunted part of the pipe, hence the reading of the ammeter will give the current *I* in the pipe. The current may be said to have been sucked out of the pipe by the battery, and made to flow through the ammeter, where it can be measured; as far as the current in that short section is concerned the pipe circuit has in effect been electrically cut in two as though an insulating joint had been introduced.

If *D* is a galvanometer with proportionate deflections, instead of a mere detector, then by taking a deflection immediately after the shunt circuit has been opened a reading proportionate to the drop of voltage for that current will be obtained. The instrument *D* is thereby calibrated to read the pipe currents directly and can be used for this purpose thereafter; the test with the battery current is therefore merely of the nature of a preliminary calibration, and need be carried out only once for each station.

A number of modifications of this method are described in Hering's paper. The chief advantage claimed for this method as

compared with plain drop of potential method described above is that it eliminates the uncertainty of the resistance of the pipe and therefore gives greater accuracy. It is very doubtful, however, whether the complication of the additional apparatus is justified except in special cases. As previously stated, the resistance of the pipe can be definitely determined from the tables with an accuracy of about 10 per cent, and the extremely variable current that is usually found on pipes can hardly be averaged with greater precision than this. Moreover, since the millivolt drop being measured in any practical case is usually very small (generally less than 1 millivolt), quite appreciable errors would be introduced due to thermoelectromotive forces in the millivoltmeter circuit itself. A difference of 3° or 4° in the temperature of the junctions would produce errors amounting to several per cent or larger, and this difference might readily occur, especially in gas pipes when the pipes are excavated and one terminal is more or less damp and others relatively dry. Further, the temperature coefficient of iron pipe, particularly wrought iron or low carbon steel, is very high, and seasonal changes in temperature of the pipe will produce variations of 5 to 10 per cent in the resistance. It appears, therefore, that accurate calibration of the pipe is very rarely justified in view of the complications of the apparatus required for this purpose.

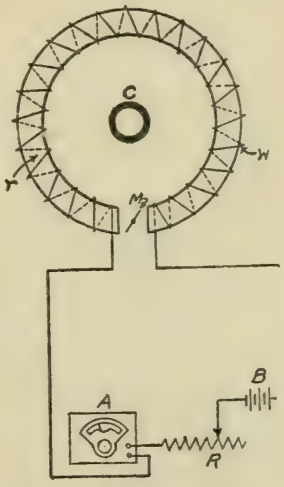

FIG. 11.—*Diagram of D. C. ratio relay*

(*c*). USE OF THE DIRECT-CURRENT RATIO RELAY.—The use of the direct-current ratio relay for measuring current in conductors which can not be opened for the insertion of ammeters or shunts has only recently been employed. The ratio relay permits the measurement of variable continuous currents of any magnitude by means of a small capacity D. C. ammeter. In its fundamental principle of operation the relay consists of a split iron ring r, shown in Fig. 11, which is slipped over the conductor C, the current in which is to be measured. The iron ring need not be laminated, and it carries a secondary winding W consisting of a large number of turns of fine wire in series with a low-voltage battery B, a variable resistance R, and a direct-current ammeter A.

In the gap between the poles of the split ring is placed a small electromagnet M. Current in the conductor C sets up a magnetic flux in the iron, which may be neutralized by a current in the auxiliary winding W from the battery B. When this neutralization occurs, as indicated by the small electromagnet, the ampere turns of C and W are equal and the current in C is read on the ammeter A, the reading being multiplied by the ratio of the turns W to the turns C, which latter in the case of the pipe is unity. This ratio relay is manufactured in two forms, in one of which the secondary is made to follow automatically the fluctuations of the line current C. In the other form, known as the D. C. line current-testing set, the current in the secondary is controlled by the observer. A complete circuit diagram for the automatic instrument is shown in Fig. 12. In this form any magnetism due to unequal primary and secondary ampere turn causes a deflection of the electromagnet M, which in moving will open or close a relay contact K. If the primary ampere turns are in excess K closes, the relay P is energized, and its plunger presses against the action of a spring, a small carbon pile rheostat R causing the secondary current to increase until the secondary ampere turns are slightly in excess, when the contact K opens. When the current in the relay D is kept at K the plunger of the relay P recoils. The resistance of the carbon pile R, whose plates are immersed in oil, increases, and the secondary current falls until the contact at K closes again. Thus there is maintained in the secondary circuit a pulsating current, the average value of whose ampere turns is exactly equal to the ampere turns of the conductor C. The principle of operation is thus quite similar to that of the Tirrill regulator.

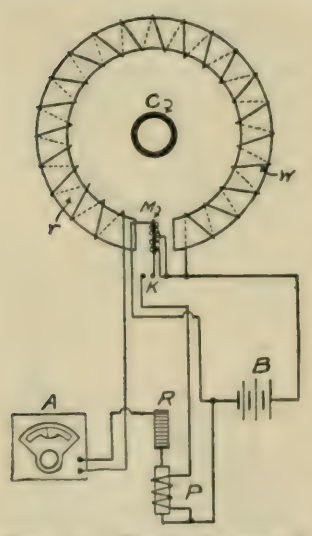

FIG. 12.—*Circuit diagram of automatic D. C. ratio relay*

As these instruments are made commercially two iron cores are provided in connection with the current ratio relay. One is large enough to encircle a conductor up to about 3½ inches diameter, and the other large enough to encircle a conductor up to about 15 inches in diameter. This core is hinged so that it can be placed

around pipes of large diameter. Larger sizes can be provided, if desired.

In order to measure the current in any conductor such as a pipe line, relay, or bus bars, open the hinge core and close it around the conductor. Insert the contact plug so that the current enters the core from the side marked with a cross. After that press the button on the left-hand side of the instrument box and the ammeter will at once show the current flowing in the conductor. Should the direction of the current be unknown, insert the plug either way and if no reading is obtained reverse the plug, whereupon the current flowing in the conductor will be indicated. This instrument will measure current from about 2 per cent of its full rated load up to 100 per cent of the rated load. It can be secured for any desired maximum rating.

The instrument just described, which is automatic in its operation, is most convenient for the measurement of rapidly fluctuating currents such as usually found on pipe systems. It is practicable, however, to use a simpler form known as the d. c. line current-testing set. This differs from the ratio relay in so far as it does not work automatically, but the rheostat which regulates the secondary current to balance the primary magnetizing force is operated by hand. A signal lamp is provided showing when the ampere turns in the secondary coil are in excess of those of the primary, and this instrument can be used very well where the changes of current are not too rapid and where only approximate results are desired. The nonautomatic instrument is simpler in construction, cheaper, and considerably lighter in weight than the automatic relay, and it would often be useful for purposes of electrolysis measurements. This instrument can be used for making current measurements of from about 10 amperes up to any higher value, although the accuracy on a 10-ampere setting would not be very great. This instrument is considerably more convenient to use than the divided-circuit method described above and should prove quite useful where for any reason it might be necessary to get a more accurate measurement of the current than is practicable with the ordinary drop of potential method. It can also be used in connection with the drop of potential method for the purpose of calibrating the pipe; that is, for measuring the resistance of any particular portion of it. This apparatus is manufactured by the Weston Electro-Mechanical Co., of Oakland, Cal.

(*D*) **Current Leakage Measurements.**—It is often desirable to measure the amount of current which is leaking off from a pipe within any given area in order to get an idea as to the general average rate of corrosion within this area. In general, three methods of measuring the intensity of leakage current are available, namely, (1) by differential current measurements—that is, by measuring the current flow in the pipe at both ends of the section within which the leakage is to be determined and taking the difference between the readings as the total leakage within the section in question—(2) by the use of the Haber earth current collector; and (3) by the measurement of polarization potentials.

(*a*) Differential Current Measurements.—The first of these methods can be used advantageously where the section under investigation offers a large area for leakage and where conditions are such that the total leakage of current is large. In this case an accurate measurement of the current flow at the two ends of the section can usually be made to yield a fairly accurate value of the total leakage sought. In work of this kind, however, it is not sufficiently accurate to use the drop of potential method of measuring current, but either some form of the divided circuit method described above, or a d. c. ratio set should be used. The latter is, in general, to be preferred, because of its greater convenience and high accuracy. In making measurements of leakage currents by this method it is necessary to make sure that there are no branches in the pipe or other metallic connections by which current may be carried away from the pipe within the section under examination.

(*b*) Use of the Haber Earth Ammeter.—The Bureau of Standards has experimented with a number of modified forms of this apparatus, the various modifications used being designed to reduce to a minimum the errors accompanying its use. The type that we have found most satisfactory consists of a plate of glass or mica inside of an insulating tube, the inside diameter of which about equals the diameter of the insulating plate, and in our work we have generally used a diameter of 10 cm. (4 inches) and a length of about 10 cm. also. On either side of the insulating plate is placed a thin copper disk from which insulated leads are brought out to connect to a milliammeter. On the outside of the copper plates are placed thin layers of some porous material saturated with strong copper-sulphate solution to prevent polarization. For this purpose one or two heavy sheets of blotting paper

soaked in a saturated solution of copper sulphate has been found very desirable. Outside of these layers of blotting paper the insulating tube is filled in with earth taken from the excavation in which the current is to be collected. It is very important that the earth be packed into the collector as soon as taken from the excavation so that the moisture content will be the same as that in the earth which is to be filled in around the collector; otherwise, the resistivity of the earth in the collector may be greater or less than that of the earth surrounding the collector, in which case the instrument will read in error. In practically all cases we have found that because of the high conductivity of the copper plates and the strong copper-sulphate solution on either side of them, the density of current inside the collector is greater than in the region surrounding it, so that there is a general tendency for the ammeter connected to the leads to read too high, and we have had to overcome this by putting a proper amount of resistance in series with the ammeter. The amount required varies according to the design of the collector and the relative resistivity of the earth inside the collector and that surrounding, and it should be determined for each particular design of collector and for the average conditions under which it is used.

The errors due to the above cause, however, are generally rather small compared to other sources of error, chief of which is the unequal distribution of current discharge from pipe surfaces in actual practice. We have found that the current discharge over any considerable portion of a pipe surface is very nonuniformly distributed, and a current collector placed at one point of a line might show a very heavy current discharge from the pipe, but when moved a foot or two away might show practically no current. For this reason we regard the earth collector as of very little value except for very special kinds of electrolysis survey work, and we rarely use it where the object of the survey is merely to determine the general electrolysis conditions existing in any particular case.

(*c*) Polarization Potential Measurements.—A method that has been proposed for determining the intensity of leakage current on the surface of the pipe at any point is that of measuring the polarization potential at the surface of the pipe. This method has been used to some extent abroad, but has found practically no application in this country.

The polarization voltage at the surface of an electrode is *the change in voltage between an electrolyte and electrode immersed therein*

due to the flow of electric current to or from the electrode. In a great many electrolytes, including some soils, this change in voltage, or the polarization potential, soon reaches a steady state after the application of a current, and the magnitude of the polarization potential is nearly proportional to the intensity of the current flowing. Under such conditions if the potential difference between a pipe and an electrode buried in the soil adjacent thereto be measured at a time of the day when no current is flowing from or to the pipe and again at a time when there is current flowing to or from the pipe, the sign and magnitude of the change of voltage will give a fair idea as to the intensity of the current discharge at the point under consideration. However, in many electrolytes and in certain soils the polarization potential is not by any means proportional to the intensity of the current flowing, so that unless extraordinary care is exercised the results of polarization potential measurements may be decidedly misleading. The variations that may be expected under certain conditions are discussed in another publication of the Bureau of Standards.[1]

The method of polarization potential measurement has the further disadvantage which is common to the use of the Haber earth ammeter as mentioned above, namely, that even if conditions are such as to make the measurement a correct one, it gives only a local value of the current leakage and a very large number of such measurements would have to be made in order that any adequate idea regarding the rate of damage on the pipe could be determined. Further, this method requires two measurements, one of which must be made when it is known that substantially no current is flowing so that it is often quite inconvenient to use.

It will appear from the foregoing that measurements of leakage currents are usually unsatisfactory, not only because of the difficulty of making accurate measurements but because, owing to the irregular and uncertain character of the distribution of the leakage, the measurements when made are of doubtful value.

III. MISCELLANEOUS MEASUREMENTS

1. LOCATION AND TESTING OF HIGH-RESISTANCE JOINTS IN PIPES

In making electrolysis surveys it not infrequently becomes necessary to determine whether or not there are any considerable number of high-resistance joints in certain portions of the pipe system. For example, if it is contemplated to install a pipe-

[1] McCollum and Logan, Technologic Paper No. [illegible] this bureau.

drainage system on a large cast-iron main, this should not be done until it has been definitely determined that there are no high-resistance joints in that portion of the line in which heavy currents would be caused to flow by the pipe drainage. Also in case it is not definitely known that heavy currents are flowing in any important main it may often be desirable to determine whether or not there are any high-resistance joints, since the presence of such joints in a main carrying heavy current is likely to give rise to serious corrosion on the positive side of the joint. If such joints are found, it is important either to prevent the current from flowing in the pipe or else to bond over the joint so as to minimize the trouble as far as practicable.

High-resistance joints in pipes are most conveniently located by means of potential gradient measurements along the pipes. It is generally best to begin by taking potential difference measurements between accessible points a considerable distance apart, such, for example, as between adjoining fire hydrants or between service connections 100 feet or more apart. Wherever such connections are not readily available, it is entirely feasible to drive holes in the ground above the pipe with a bar or auger and insert in these holes nonpolarizable electrodes, such as described in the previous part of this paper, and measure the potential difference between them after the manner already outlined. It is unnecessary that these holes should be drilled down to the surface of the pipe, but if the holes terminate anywhere within a foot or two of the pipe, they would generally suffice. It is not therefore necessary to locate the pipe with great precision. Measurements are taken between points thus located throughout the length of the pipe that is to be explored, and if there are any resistance joints in the pipe it will be found that the potential-drop readings at certain places will be larger than others, it being assumed of course that potential readings are taken at each point for a sufficiently long period to get a fair average value. The time required will vary from two or three minutes to half an hour according to whether the schedule is frequent or infrequent or whether the current in the pipe is being affected by the cars in a large territory or only by those on a single portion of the line. After going over the line in this way, taking potential-difference measurements between points a considerable distance apart, those sections which show high readings are then explored in more detail in a similar manner by placing the electrodes closer together, and in this

way the location of the high-resistance joint can be definitely determined.

When the location of the joint has been determined it is usually sufficient to measure the drop of potential across the joint and also determine approximately the conductivity of the soil in the vicinity, and from this it can be determined with sufficient accuracy whether the pipe is in serious danger at that point. If the earth resistance is low—such as, for example, a few hundred ohms per centimeter cube—then a drop of potential of 0.1 volt across an ordinary joint should be considered serious; but if the resistance of the earth is very high under average moisture conditions—say, 10 or 15 thousand ohms per centimeter cube or more—a potential drop of several tenths of a volt on a heavy cast-iron main will usually be permissible, although in the case of a wrought iron or steel main a considerably lower value should be maintained. If it is desired to measure the actual resistance of the joint in terms of a given length of pipe, this can be done very conveniently by means of the principle of the Wheatstone bridge, as shown in Fig. 13, in application to rail joints. Here the joint being tested forms one arm of the bridge and a measured length of the pipe a second arm, and two resistances M and N serve as the other two sides of the bridge. The current in the pipe suffices for the test current. It is only necessary to adjust M and N so that the galvanometer or millivoltmeter reads zero, and then the resistance of the joint in terms of a known length of pipe can be determined from the bridge setting.

2. TRACK TESTING

(*A*) **Kinds and Character of Track Tests.**—The need for making electrical tests on railway tracks is, in general, twofold. First, to locate the cause of any bad electrolysis conditions that may have been previously encountered; and, second, to serve as a guide for the systematic maintenance of track bonding and return feeders, and in some instances to determine the need for additional feeders. The track tests usually consist either in measuring the current density in the tracks at various points or in testing the condition of the bonding of the joints and the cross-bonding between tracks. Measurement of current in the tracks is made only when it is desired to find out whether or not additional return feeders are required to prevent excessive track drop even on a well-bonded track. These current measurements are made by the drop of potential method the same as described above for

determining the current flow in pipes or by means of the direct-current ratio relay, also described above. The most frequent measurements, however, are the tests of the bonds and cross bonds.

(*B*) **Methods of Testing Bonds.**—There are three methods in use for testing the condition of track bonds as follows:

(*a*) Examination by Inspection.—This method of testing bonds by simple inspection is one which had much greater vogue in the past than at the present time, but it is unfortunately, even now, too frequently depended upon. It consists usually in going along the track and making superficial inspection of the bonds, and if they appear to be mechanically good, the assumption is made that bonding is in satisfactory condition. Not infrequently this inspection is not made except when snow is on the track with a temperature not much below freezing, in which case the man goes

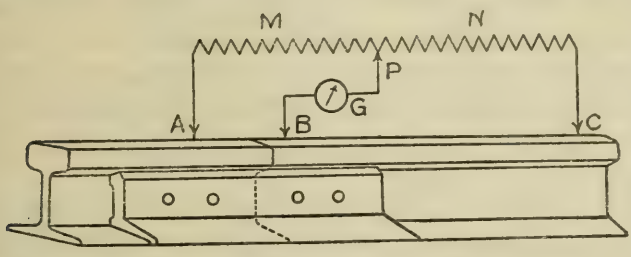

Fig. 13.—*Diagram of circuits in portable bond tester*

along the track and wherever the snow is found to be melting adjacent to a bond the joint is listed for rebonding. This crude method of bond testing can not be too severely condemned. A joint that appears to be mechanically perfect may have a high electrical resistance, due to corroded contacts, which corrosion may not be evident through superficial inspection, and joints may have a sufficiently high resistance to increase the total track resistance several fold without generating sufficient heat to melt snow around the joint. Any examination of bonds by simple inspection should, in general, be regarded as a very poor makeshift and some more accurate method should be used wherever practicable.

(*b*) Use of Portable Bond Testers.—There are in use at the present time a number of portable bond testers operating on the principle of the slide wire bridge, a portable millivoltmeter being used to determine when the bridge is balanced. The principle of operation is essentially similar to that shown in Fig. 13, for the

measurement of the resistance of a high-resistance joint in the pipe. These instruments indicate the resistance of the joint in terms of the resistance of a definite length of rail. One man can operate a testing set of this kind when necessary, although a man with a helper to handle the contact terminals can work somewhat more conveniently and more rapidly. This method of testing, while somewhat slow and tedious, is in most cases about the most economical method of testing bonds.

(*c*) BOND TESTING BY MEANS OF SPECIAL TEST CAR.—A method that has been used to a considerable extent during the last few years for testing bonds of railway lines is what is known as the "autographic method." This method is like that of the portable bond tester above described and is based on the comparison of the potential drop across a certain length of rail, including the joint with that across an equal length of adjacent solid rail. The two readings are taken and autographically recorded within a fraction of a second; during this short time the variation of the current in the rail is so small that it generally can be neglected, so that the potential drop will be proportional to the resistance. Should, however, a change of current occur, it is shown on the record and due allowance can be made.

General description.—The complete recorder consists of the following principal parts: (1) Recording table, containing necessary measuring, recording, and locating devices, also controlling apparatus for a motor generator set and storage battery; (2) motor generator set consisting of a 600-volt motor directly connected to a low-voltage direct-current generator capable of supplying a local testing current of approximately 500 amperes; (3) storage battery supplying the energy for the spark and auxiliary circuits and the motor which drives the roll of paper on which the record is made; (4) test truck maintaining the necessary contact brushes, interrupter for spark circuit, and contactor for paper drive motor.

The three first mentioned are installed in the temporary test car and the test truck is attached to the car. On high-speed roads where the operation of the test truck would be inconvenient the brushes are mounted on the temporary test car. The measuring instruments are Weston millivoltmeters, one for each rail, provided with a special wire scale which connects with a spark coil. A wire is leading from each division of the scale to the spark cone; the record passes between this spark cone and a bar connected to the spark coil. For each discharge of the spark coil the current pierces the chart at a place corresponding to a position of the

millivoltmeter handle; the discharges are so frequent that every move of the handle is recorded. By means of an electric motor connected with a contactor on a wheel on the test truck the chart is moved proportionally to the distance traveled by the truck.

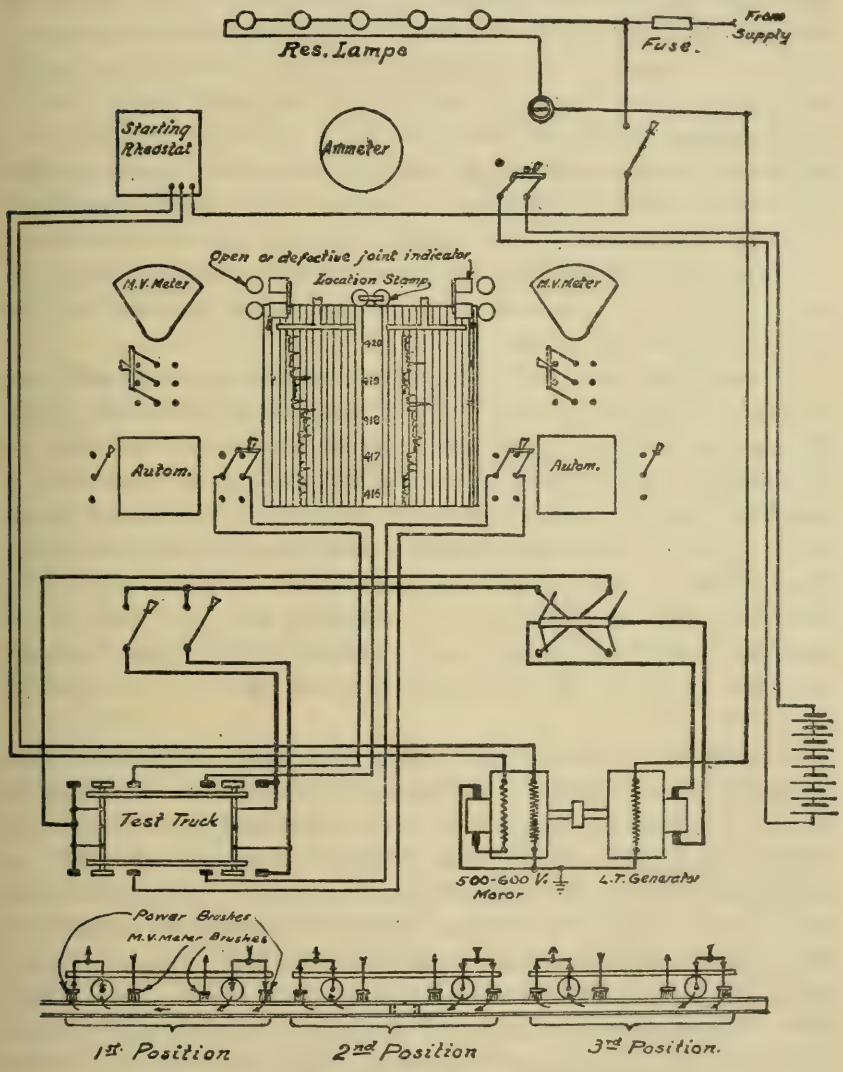

FIG. 14.—*Diagram of external connections of test car*

One inch of record represents 64 feet of track. The diagram in Fig. 14 shows the external connections of the recorder. The local testing current is conveyed to and from the rail by means of the contact brushes, and in a similar manner the connection of the

millivoltmeter is brought in contact with the rail. In order to eliminate thermoelectromotive forces the brushes are of steel similar to the rail.

Method of Operation.—When the test truck is moving along the track the successive positions of the brushes will be those indicated at the bottom of the diagram. The first shows the potential brushes spanning a certain length of solid rail, while in the second position they span an equal length of rail, including a joint, and in the third they again span the solid rail. While the brushes have had these positions every movement of the millivoltmeter needle has been recorded on the chart by means of the electric sparks.

Should the potential drop exceed the limit of the instrument, which is 110 millivolts, the instrument will be automatically protected during the overload, this incident being recorded on the extreme edge of the record.

Although the speed of the paper is proportional to the distance traveled, it is usual to take frequent locations of landmarks along the route in order that more exact locations of bad joints may be determined. At frequent intervals the local testing current is withdrawn and the amount and direction of the rail current noted on the record. From the change in the potential drop the direction and the amount of traction current can be determined. By connecting one instrument as a voltmeter and the other as an ammeter a continuous record can be obtained of the trolley voltage along the line and the transmission losses can be calculated for any desired point.

Advantages of Autographic Test.—Among the advantages claimed for this method of testing are the following: (1) A special test current is employed in the joints under test, so that there is always ample drop of potential to give a definite indication on the record; this avoids the difficulty frequently met with in the use of bond testers of insufficient traction current to give a definite indication on the testing instrument, which may give rise to frequent and prolonged delays on the part of the tester; (2) it eliminates the personal element; (3) it gives an autographic record which can be filed as a permanent record of the condition of the track at the time of test; (4) a large amount of track can be covered in a short time, so that a test of the entire road can be quickly made at any particular period.

The cost of testing bonds by this method depends upon the locality and local conditions, but in general it is somewhat greater

than the cost of manual testing with the usual portable bond tester. This apparatus is manufactured and operated by the Maintenance Improvement Co. (Inc.), 14 Church Street, New York City. A number of railway companies have designed and used test cars of various descriptions for the testing of rail bonds, but the detailed description of these is beyond the scope of this paper.

Practice regarding the maintenance of track bonds varies considerably, and different companies permit widely varying resistance in bonds before considering them in need of replacement. In the majority of cases, however, a joint which has a resistance greater than 6 to 10 feet of rail is regarded as defective. This subject is discussed in detail in another publication of the Bureau of Standards.[2]

(*d*) Testing of Cross Bonds.—In addition to testing the joint bonds above referred to it is important also to test periodically the condition of cross bonds. This can best be done by means of a low-reading voltmeter having a range not exceeding about 1 volt, the method being to go along the track and at frequent intervals measure the potential difference between the two rails of the single track and also between the tracks of the double-track line. It is permissible, as a rule, to have considerably higher potential drops between rails and tracks than would be allowed on a single joint, but in general, the drop of potential between rails in any particular location should not be greater than about 0.1 volt.

(*e*) Periodic Testing of Bonds.—It is highly desirable for the purpose of permanently maintaining good electrolysis conditions to adopt the practice of testing periodically all bonds and cross bonds on a railway system. If the track is once placed in good condition and the roadbed is, in general, of substantial construction so as to prevent excessive mechanical strains on the joint due to passing traffic, the testing of bonds about once a year will probably be sufficient under most conditions. Where, however, the joints are known to be deteriorating rapidly and particularly where the roadbed is such as to allow considerable movement of the joints under the weight of traffic, much more frequent bond testing will be necessary if the track is to be maintained at all times in reasonably good condition.

[2] E. R. Shepard, Modern Practice in the Construction and Maintenance of Rail Joints and Bonds in Electric Railways, Technologic Paper No. 62, this Bureau.

3. MEASUREMENT OF EARTH RESISTANCE

In connection with any extensive electrolysis survey it will, in general, be desirable to take a considerable number of samples of earth from widely scattered points throughout the area under investigation and measure the resistivity of these samples. This data is often desirable to assist in the interpretation of the electrical tests made in connection with the survey, since if the earth resistance is, in general, very high it will be safe to permit higher potential drops between various points of the pipe networks than would be safe if the earth resistance were found to be, in general, comparatively low. The methods for measuring earth resistance and the conditions under which tests should be made are set forth in detail in another publication of the Bureau of Standards.[3]

4. MEASUREMENT OF LEAKAGE RESISTANCE BETWEEN RAILWAY TRACKS AND EARTH

(*A*) **Importance of Tests.**—The determination of the average resistance of the leakage path between railway tracks and surrounding earth is often very desirable, particularly where it is necessary to determine what over-all potential drops may safely be permitted in the track return. It will be evident that if the resistance of the leakage paths is very high it will be safe to allow higher potential drops on the track than if the leakage resistance be low, although the voltage drop which may be considered safe is not directly proportional to the average resistance of the leakage path. The relation between these is discussed in detail in another publication of the Bureau of Standards.[4]

(*B*) **Method of Testing.**—The Bureau of Standards has given considerable attention to tests of this character and still has the subject under investigation. A considerable number of tests on various types of roadbeds have been made, during the course of which two methods have been found satisfactory. One of these methods consists of inserting insulating joints in the track at two points distant 1000 feet or more apart and bonding around these with a heavy bond designed to be conveniently opened at any time for testing. The test is made at night when no traffic is on the line, the shunt around the insulating joint being opened and then a low-voltage battery applied between the isolated section of track and a suitable earthed terminal giving a very low resistance to ground. For this purpose the railway track on either side of

[3] McCollum and Logan, Technologic Paper, No. 26, this Bureau.
[4] McCollum and Logan, Technologic Paper, No. 61, this Bureau.

the isolated section can be used. These tracks have substantially the potential of a point on the earth quite remote from the track section under test. When this connection is made the current flowing from the battery to the isolated section of track must practically all pass off through the track roadbed in this section, the leakage around the insulating joints being very small compared to the total leakage through the roadbed of the section under test; and this current is measured simultaneously with the potential difference between the track and a second earth terminal which should preferably be remote both from the isolated track section under test and from the earth terminal which is carrying the cur-

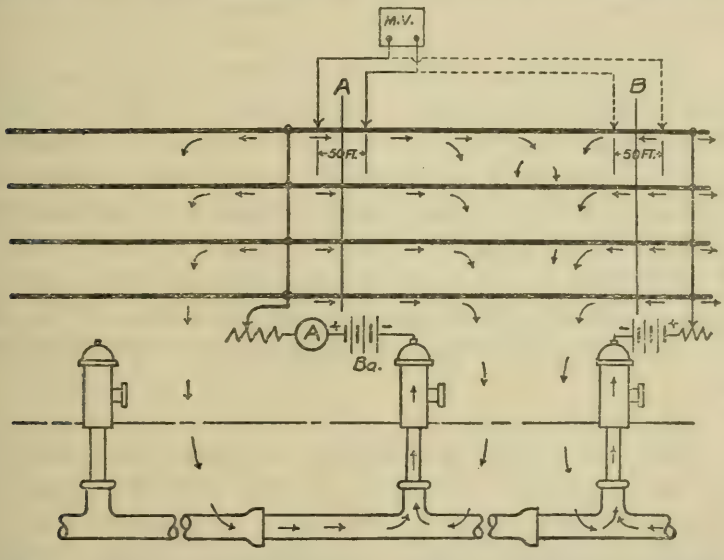

FIG. 15.—*Diagram of connections between a double-track railway line and adjoining pipe syestem, for measuring leakage resistances of a section of roadbed*

rent of the battery. The resistance of the leakage path between the isolated track section and ground is then calculated from the ammeter and voltmeter readings.

The second method of testing which has given satisfactory results in some cases eliminates the necessity of inserting insulating joints in the track, a procedure which is often quite difficult, especially where cross bonds or space bars are frequently used, In this method two batteries are required and the arrangement is shown in Fig. 15. The batteries are stationed from one to several thousand feet apart and connected as in the preceding test, one terminal being connected to track and the other to an earthed terminal some distance away. It is desirable to connect the

positive terminal of both batteries to the track and the negative terminal to earth, since this represents the polarity existing in practice where a current is leaking from the track into the earth. From an examination of the figure it will be seen that a great deal of current flowing from each battery will flow off in the directions away from the section under test, as indicated by the arrows, but a certain amount, corresponding to the total leakage of the current on the section between the batteries, will flow into this section. If now we measure the millivolt drop on a short length of the rails at the points *A* and *B*, just inside the points at which the batteries are connected to the tracks, we can calculate from this millivolt drop on a measured length of rail of known weight the approximate current which is flowing into the section under test from each end. The sum of these two currents will then be the total leakage current from the test section. At the same time a voltmeter is used to measure the potential difference between the section under test and a remote point in the ground, as at *E;* and from this voltmeter reading and the total leakage current the resistance of the section can be calculated. If high accuracy is sought, the rails must be calibrated by one of the methods described above for calibrating pipe in order to secure an accurate value of the resistance. This refinement, however, is unnecessary in practically all cases.

A considerable number of measurements of this sort have shown that, in general, the leakage resistance of 1000 feet of single-track roadbed of ordinary type will be found to range between 0.3 ohm and about 6 to 8 ohms. In general, in concrete roadbeds and others in which the rails are thoroughly embedded in the earth the leakage resistance is quite low; whereas where the track is so constructed that the rails are entirely out of contact with the earth and the ties set on well-drained rock ballast, the leakage resistance is very high. It is obvious that, in view of this very wide range of roadbed resistance, it would be absurd to limit the permissible voltage drop in any section of track to the same value, regardless of its resistance. Hence it is important to determine the approximate roadbed resistance in various portions of a railway system before a strictly logical limitation of voltage drop could be prescribed. It is most important, and in general would be sufficient, to determine the leakage resistance of the tracks at a few points in the system in outlying regions where the current tends most to leak off the rails and also in the region near the power house where current is returning to rails, care being

taken to select representative types of construction. An experienced engineer can usually form a fairly accurate judgment regarding the leakage resistance of a railway roadbed by inspection of the line or by an examination of the specifications under which the road was constructed, so that where only a rough estimate is required an actual measurement of the leakage resistance is not necessary.

5. DETERMINATION OF THE CAUSE OF CORROSION

There is a very common impression extant that the final products of the corrosion of iron when due to stray currents are the black oxides, whereas in the case of self-corrosion the red oxide is produced. Numerous investigations have been made with a view to determining whether or not this is true to any appreciable extent. These investigations are described in some detail in Technologic Paper 25 of this Bureau. In these experiments it is shown that when iron corrodes, whether due to electrolysis from stray currents or to local galvanic action, the first product of corrosion is usually the hydroxide of iron or some other soluble salt of iron, depending on the constituents of the electrolyte in the soil. When these come in contact with the oxygen usually prevalent in soil waters an insoluble precipitate of iron oxide is formed. If the rate of corrosion is relatively rapid and the concentration of oxygen relatively low, the tendency will be to form ferrous oxides, and there may, therefore, be expected a predominance of the black magnetic deposit often mistakenly called graphite. If, on the other hand, the rate of corrosion is relatively low and there is an abundant supply of oxygen in the soil water, the tendency will be for the ferric or red oxide to predominate. In most soils the amount of oxygen that can come in contact with the dissolved iron salt is usually quite limited, so that where the corrosion is very rapid there will be a definite tendency toward the formation of the black oxide. As a rule, especially in severe cases of electrolytic corrosion, the corrosion takes place much more rapidly than in the case of soil corrosion, so that, in general, we would expect the black oxide to result from corrosion due to this cause, whereas in the majority of cases, due to the slowness with which self-corrosion proceeds, we would expect a predominance of red oxide. This rule is by no means infallible, however, because electrolytic corrosion sometimes takes place more slowly where the current discharged from the pipes is very small, and further special cases arise in which self-corrosion proceeds with great ra-

pidity, as, for example, in certain acid soils or in soils in which cinders, furnace slag, or other foreign materials exist which may form galvanic couples when in contact with iron. In such cases the end products of self-corrosion may be black oxides and appear identical in every respect to the end products of electrolytic corrosion. It is therefore impossible to tell with certainty from the examination of a corroded pipe whether or not the corrosion has been caused by stray currents. Nevertheless, wherever a large preponderance of the black or magnetic oxide exists it may usually be regarded as a good indication that the rate of corrosion has been so great as to make it probable that stray currents have been largely responsible, unless corrosion tests under the same conditions which exist locally show that self-corrosion can take place with great rapidity. At the present time the only certain way of determining whether or not stray currents are causing corrosion in a particular case is to make proper electrolytic tests to determine whether the pipes are actually discharging current into the earth. In a case where serious corrosion has been caused by stray currents, and the cause of the stray currents later removed, the only way of determining whether the previous corrosion was caused by stray currents or by local influences is to make actual corrosion tests in the soil under the same average conditions of moisture and using the same kind of iron as was previously found corroded. In the absence of a test of this kind it is not possible at the present time to fix with certainty the cause of the damage.

6. DETERMINATION OF THE SOURCE OF STRAY CURRENTS

Cases frequently arise in practice where it can be easily established that pipes or other underground structures in a given locality are being damaged by stray currents, but the question arises as to the source of the stray current which is causing the trouble. This question arises frequently where two or more electric railway systems operate with grounded return in the same or near-by districts. There are, in general, two ways of determining the source of the stray current under such conditions. One method consists essentially in connecting voltmeters, preferably recording voltmeters, between the pipes or other structures which are discharging current into the earth and some other structure into which the currents are being discharged, which latter may be an auxiliary earth terminal if desired, and then shutting down momentarily first one and then another of the

railway power houses and determining the effect of this on the reading of the voltmeter. In case the shutting down of one railway system makes practically no difference in the voltmeter reading, while the shutting down of the other results in marked reduction of the reading of the instrument, it indicates quite definitely that current from the second system is the one giving rise to the trouble.

Another method which may often avoid the necessity of shutting down the power houses even temporarily consists in connecting one recording voltmeter in a suitable manner to the pipe structure, as described above, and connecting other recording voltmeters between the railway tracks and earth in all those sections of track which are known to be strongly positive to earth, and therefore discharging current into the earth. These instruments are allowed to run for a considerable period, preferably for several hours, and the shape of the curves giving the potential-difference readings at different points on the railway system are compared with the shape of the voltage curve obtained in the underground structure under investigation. If the potential difference between the injured pipe and the earth varies widely and in a substantially similar manner, as potential difference between the tracks and earth in any particular section of the railway system, it affords a definite indication that it is the leakage of the current from this section that is giving rise to most of the damage. Sometimes it will be found that the damage in a given locality is caused chiefly by the leakage from a single railway line or section of line, in which case the investigation is considerably simplified. More frequently, however, the corrosion at any point may be affected simultaneously by the leakage of current from a number of railway lines. Usually an examination of the local system will show which lines are likely to be affecting the district under investigation, and where two or more lines appear to be thus involved it is necessary to combine the readings of potential difference between tracks and earth of all of these lines, thus giving a composite leakage curve, which is to be compared with the curve of potential difference on the pipe structure under investigation. As a rule, it will be found that enough disturbing influences are at work so that the potential-difference curves will not be of exactly the same shape, but it is usually possible to show whether or not they tend, in general, to increase or decrease simultaneously, and in the majority of cases the source of the greater part of the stray current can be definitely determined in this way.

7. LOCATING CONCEALED METALLIC CONNECTIONS

During the course of electrolysis surveys it is frequently necessary to locate concealed metallic conductors such as buried cross bonds in the tracks, metallic connections between the pipes and railway negative return, or even to determine the exact location of pipes themselves where such location is only approximately known. The most frequent and difficult case encountered is the location of unknown metallic connections between pipes and railway return. To locate these with a minimum of time and effort three classes of measurements are generally made.

(1) Potential-difference measurements between the pipes and railway tracks are made, and where these are much smaller than would be expected from over-all potentials and potential gradients which have been found to prevail throughout most of the railway area, it indicates a strong probability of the existence somewhere of metallic connections between the pipes and railway negative return. These may not, however, be directly between the pipes and tracks, so that potential-difference measurements made at various points along the track will not reveal even the approximate location of such connections. Their existence having been established with considerable probability by the potential-difference measurements, the next step is to measure potential differences between fire hydrants or, in the case of gas systems, between gas-service connections several hundred feet or so apart. The first such measurement will show in which direction the current is flowing in the main to which the hydrants or services are connected, and then the tester should proceed along the main in the direction in which the current is flowing and take a similar reading a few hundred feet farther on. In general, it will be found that the current will be flowing from all directions toward the point at which the metallic connection sought is made to the pipe, so that if the tester continually proceeds in the direction of current flow, he will ultimately come to a point at which the direction of current flow is reversed, and in a very short time he can almost always locate the connection within 200 or 300 feet. It can often be much more closely located by measuring potential differences between adjacent house services, it being possible in this way usually to locate the connection within 30 or 40 feet. This, however, is not close enough to make it economical to find by it excavation, but an exact location can now be determined by the use of a special exploring coil similar to that used by telephone com-

panies for locating crosses in telephone circuits. The principle of this is shown in Fig. 16. In this figure let A and B represent a railway and pipe system which are connected at some point by the buried metallic conductor C, the location of which it is desired to find. A special high-frequency buzzer or other interrupting device D is connected between the two pipe systems at any convenient point, a battery being in series with the interrupter. This can be made to send an intermittent current between the systems A and B, a portion of which will return by way of the metallic connection C. An exploring coil connected to a telephone receiver, if carried along the surface of the earth in the vicinity of the pipes A or B, will give a sound in the telephone receiver when brought near the buried conductor on which the intermittent current is flowing, due to the electromagnetic induction in the exploring coil. If the plane of this coil is parallel to the direction of

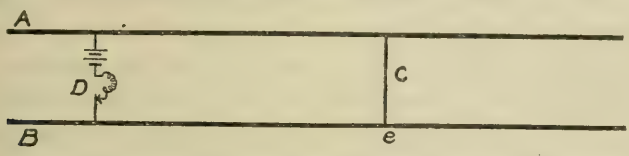

FIG. 16.—*Diagram of connection for locating concealed connection between buried metallic structures*

the conductor B, for instance, the intensity of the sound will be a maximum. If now the tester holds the telephone to his ear and proceeds along the pipe B, always keeping in such position that the intensity of the note in the receiver is a maximum, he will follow the course of the pipe system until he comes to the point E at which the metallic connection is attached, and as he proceeds farther there will be a sudden diminution in the sound in the telephone receiver. By then moving at right angles in either direction he can soon pick up the course of the connection C and trace it across to the other pipe system A. The hidden connection can then be uncovered and removed if desired. By following this procedure it is usually possible to locate a hidden connection within two or three hours, although in some cases where very complicated underground networks exist there may be so many disturbing influences and parallel paths for the current to follow that the definite location of the desired cross connection may be extremely difficult.

8. EXAMINATION OF CONCRETE STRUCTURES

In making an examination of concrete buildings, bridges, or other structures that are reported to have been injured by or to be in danger from stray currents it should first be determined whether or not the structure is of plain or reinforced concrete. If the structure contains no reinforcing material, there is no necessity of making any further investigation, because it has been definitely established that electric currents exert no deleterious effect on nonreinforced concrete.[5] If the structure in question is found to contain reinforcing material, an inspection should first be made to see whether there are any external evidences of injury of such character as may result in some cases from the discharge of current from reinforcing material into the concrete.

The existence of electric current in any particular structure can be determined by measuring potential drops between selected points on the structure spaced a considerable distance apart. If the reinforcing material is accessible, the instrument terminals should be connected directly to it, but if the terminals of the instrument have to be directly connected on the concrete, a nonpolarizable terminal similar to that described above in this report should be used. It is important in making such measurements to bear in mind that with sufficiently delicate instruments a potential difference will be indicated between any two points selected at random on a building or any other conducting structure; but the existence of such potential differences should not be accepted as evidence that any serious stray currents are flowing. If such readings are found to be of the order of magnitude of a few millivolts they should not be regarded as of any consequence. Where, however, readings of a few tenths of a volt or more between points comparatively close together are found, the source of these had best be determined.

In general, there are three possible sources from which stray electric currents may get into a building or other structure. First, from a private power plant within the building; second, through leaks from light or power mains which enter the building; and third, from stray currents from electric railway lines. It can readily be determined which of these possible sources may be giving rise to stray currents in any particular case by connecting a voltmeter between points in the building which exhibit appre-

[5] Technologic Paper No. 18, this Bureau.

ciable potential differences and momentarily shutting down the private plant or cutting off the outside source of electrical power. If the stray current comes from either of these sources, there will be sudden changes in the voltmeter reading when the sources of supply are shut off. If switching these sources on or off makes practically no difference in the voltmeter reading, steps should then be taken to see whether or not stray currents are entering the building on the grounded circuits of railway or other power lines. Where stray currents of this kind get into the building they usually enter or leave through water or gas pipes or cable sheaths which enter the building, or in rare cases through the bases of columns or foundations. It is a simple matter to determine whether or not currents are entering or leaving the building through any metallic pipes or cables which enter the building by merely taking potential-drop readings on a short length of such conductors; and the question as to whether currents are entering or leaving through columns of the building can be determined by similarly making potential-drop measurements on a suitable length of the column near its base. If the current is found to be entering the building through pipes or cables, substantially the same amount of current may be found to be leaving through other pipes or cables at other points, in which case it would usually be improbable that any serious danger would be set up. Where, however, more current flows into the building on metallic structures than is flowing out on similar metallic structures the difference might be expected to be leaving the building through the columns and foundations, in which case some damage might result; and in such cases the simplest and most obvious remedy would be to insert insulating joints in the pipes or cables which are conveying current into the structure.

In making such investigations it should be constantly borne in mind that ordinary concrete is an excellent preventive of corrosion of embedded iron, not only as regards self-corrosion, but also as regards electrolytic corrosion, and unless the potential differences between various parts of the building are of considerable magnitude no fears should be felt regarding the safety of the structure. In particular, great care should be exercised not to be misled by the presence of inevitable galvanic differences of potential which can be found in practically every structure of this kind but which cause absolutely no harm.

Part 4.—INTERPRETATION OF RESULTS OF ELECTROLYSIS MEASUREMENTS

I. GENERAL CONSIDERATIONS

The interpretation of the results of electrolysis tests requires long experience and thorough familiarity with the subject of electrolysis from stray currents. No specific key to the interpretation of the test data can be given, but below are discussed some of the fundamental principles involved, as well as some of the difficulties encountered in making a correct interpretation of electrolysis survey data.

As a rule, no single set of readings such as over-all potential measurements or measurements of current flow in pipes can be interpreted by itself alone, but must be judged by a variety of other conditions. For instance, very high over-all potentials may at times be accompanied by, and in some measure caused by, high leakage resistance between track and ground. This resistance is sometimes so high that even very high over-all potentials would not cause sufficient current to leak from the tracks into the earth to give rise to any serious electrolysis conditions. On the other hand, where the leakage resistance between tracks and ground is very low, the current delivered to the track in outlying portions will readily leak off into the earth, thereby greatly reducing the current in the rails and correspondingly reducing the voltage drop in the track. As pointed out in another part of this report, different types of roadbeds commonly encountered in electric railway work exhibit widely different characteristics as to leakage resistance between tracks and rails, some showing a resistance many times greater than other types of construction. In some cases 50 per cent or more of the total current may return by way of the earth and pipes, thus giving rise to low over-all potential drops, whereas if all of the current was compelled to return by the rails, much higher over-all potentials would prevail, although electrolysis conditions would be decidedly better in the latter case. Hence, while high over-all potentials *under average conditions* indicate bad electrolysis conditions, nevertheless, under certain conditions where leakage resistance is very high, such would not be the case; and conversely low over-all potentials *may result from* very bad electrolysis conditions due to low leakage resistance between tracks and earth.

Similar considerations apply to potential-difference measurements between pipes and tracks. High values of leakage resistance tend, in general, to produce high potential differences, whereas if the leakage resistance is low, a much larger current may flow from pipe to tracks with even considerably smaller potential differences. Hence, potential-difference readings alone can not be accepted as an indication of the amount of current discharged, and before even approximate conclusions can be drawn from them some definite idea regarding the leakage resistance between pipes and tracks near the points of measurement must be obtained. This depends not alone on the character of the roadbed. The location of the pipes is an important factor in determining both the amount of leakage current and also the distribution of such leakage current. Further, because of the effect of location on pipes on the distribution of leakage current, it is not sufficient to determine the total amount of current which the pipes may be discharging, but it is important also to know where and how the current leaves the pipes. If a main parallel to a railway line is at all points 20 or 30 feet distant, the current discharge will generally be distributed over a large area, so that a considerable amount of current may be discharged from the pipes without serious corrosion developing at any point. On the other hand, if the pipe comes very close to the track at a few points, as, for instance, where the main or services cross directly under the track and within a few feet of the surface, the current discharge will be greatly concentrated at such points, thereby giving rise to very rapid deterioration of the pipe. Again, even though it may be determined that the current is not doing any injury to the pipes at the point at which it is leaving them, as, for example, where pipe drainage is installed and the current is practically all removed from the pipe through metallic connections, it can not be concluded that such currents are not doing any injury to the pipe system on which they may be flowing, since there are, as a rule, a considerable number of high-resistance joints in pipe systems, and these resistances may be high enough to cause considerable current to leak around the joint, thus giving rise to considerable corrosion on the positive side of the joint in many and unlooked-for places throughout the pipe system. In addition to these considerations it must be borne in mind that current flow on any one pipe system may injure not alone the pipe system on which the current is found, but it may be causing even greater injury on some other

pipe or cable system from which it may be discharging into the system in which it is actually measured. Therefore, where considerable amounts of current are found on any pipe system it is important to find out whether it is producing trouble in any other pipe system from which it may be drawn. This is particularly important in cases where pipe drainage is applied to one or more of the pipe systems in any given locality. Even if drainage is applied to all the systems, great care must be exercised not to drain one system more than another, as by so doing considerable injury to the systems of higher potential may be produced. For this reason it is desirable to measure potential differences between the different systems of underground structures occupying the same general locality, as pointed out in an earlier part of this paper.

It will be evident from the foregoing considerations that the very low potential differences in the positive areas which accompany most installations of pipe-drainage systems may induce a false sense of security unless due consideration is given to the secondary conditions which may be set up by the pipe-drainage connections.

II. THE USE OF REDUCTION FACTORS

In most cases it is not practicable to take readings of current and potentials at any point over a sufficiently long time to get a fair average value of the readings at that point. Such readings should always be taken as long as circumstances permit, but in making electrolysis surveys it is usually necessary to take a large number of readings scattered over a wide area so that each reading can be continued only for a comparatively short time. Such short-time readings can not, in general, be used directly as a basis for determining electrolysis conditions. The great variability of railway loads generally causes the readings to fluctuate decidedly from time to time and in order to interpret properly the results of the survey the readings must be reduced to some common basis as, for example, either the potential for average scheduled traffic, the all-day average, the operating-day average, the average for the maximum hour, or the maximum average value for any 10-minute period. Each of these bases has certain advantages and disadvantages depending partly on individual conditions; and the method of procedure will often differ, depending on the method to be followed in interpreting the results. All are affected by such

factors as rush or light days, unusual weather conditions, electric heaters in cold weather, morning and evening peak loads, and other causes; and these factors must be considered. Electrolytic damage is determined by average conditions over long periods, but danger from arcing and overheating are more closely related to maximum values. Since electrolytic damage is by far the most important because of its continual and universal occurrence, while only very rare cases of arcing and overheating have been observed, the average values over long periods give a much more accurate index of the seriousness of the trouble than any short-time readings.

The great unreliability of short-time readings for determining electrolysis conditions is especially noticeable when comparing the load curve of a line having a 5, 10, or 15 minute schedule with that of hourly interurban service, or when comparing that of a station having a 45 per cent load factor with one having a load factor of 10 per cent. Because of this great variation and uncertainty in short-time measurements and for the purposes of interpretation and comparison, it is desirable that all short-time readings be reduced to values for some representative period, preferably the all-day average.

(*A*) **Ten-Minute Basis.**—Some engineers prefer to determine directly the highest average value for a period of about 10 minutes and use this as an index to electrolysis conditions, while some even attach importance to momentary peak values. The maximum 10-minute potential is a peak load value and must be measured at the time of peak, it being too variable to derive from a value observed during another part of the day and corrected by means of the load curve, as suggested later for readings over longer periods. Reading the actual value with no correction from a load curve has the advantage of greater simplicity and is free from one source of error, due to the possibility of the load curve being different on the line measured from the load curve used in calculations, which would probably be that of the station supplying that line. On the other hand, the 10-minute value during peak load fluctuates between much wider limits than the average for a longer period and results from one day to another will lack concordance to a much greater extent than in case of readings taken over longer periods, due to the irregular and widely fluctuating character of the load.

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Numerous investigations have shown[6] that the actual amount of corrosion which takes place is much more nearly proportional to the average all-day load than it is to any short-time peak value. For this reason it is undesirable to place undue significance on high-peak values of voltage readings which are of short duration, provided the average value of such readings throughout the day is small. Voltage readings taken during such high-peak periods or during another hour of the day should be referred to the load curve for the district under consideration in order to determine the approximate value of the all-day average. Better still, as is pointed out above, the readings should be taken over a longer period of time where practicable.

Our experience in attempting to interpret results of surveys by means of short-time peak values has convinced us that not only is it open to objection on the ground that, even if accurately obtained, it is not a true index of the electrolysis situation, but the accurate determination of such peak values will generally require practically as much time as the taking of measurements over greater periods, such as an hour or longer. This is due to the fact that in order to make sure of getting the reading during the maximum 10-minute period of any particular day it will be necessary to continue the reading over a period of at least one-half hour and preferably longer, and further, owing to the variation of the 10-minute maximum from day to day, such readings would have to be repeated on a number of different days in order that either the highest maximum value, or the average maximum value, may be obtained.

(*B*) **Hour Basis.**—The average values of a reading taken over a period of one hour, either during peak load or for average scheduled traffic, or any time of day, gives values of sufficient length of time and reliability that they can usually be repeated from day to day with a fair degree of consistency. Some ordinances prescribe as a limiting value of voltage the average value for the maximum hour. Peak values of this duration usually occur at a fairly definite time each day so that one-hour readings during peak load can generally be determined with fair accuracy, and where measurements are being taken with a view to determine whether or not an ordinance of this character is being complied with, it would obviously be most logical to take the readings for an hour or somewhat longer during peak load. However, for

[6] Technologic Paper No. 25, this Bureau.

ordinary survey work designed to determine the actual danger which exists to the pipes the one-hour values have the same weakness, although to a lower extent, as the 10-minute maximum values possess in that they are not an accurate index to the magnitude of the danger from electrolysis. If, however, the load curve of the station or principal feeders supplying the district under consideration is at hand, a reading taken over a period of one hour during practically any time of the day will permit the ready determination of the average value throughout the entire day with sufficient accuracy for practically all purposes. In gen-

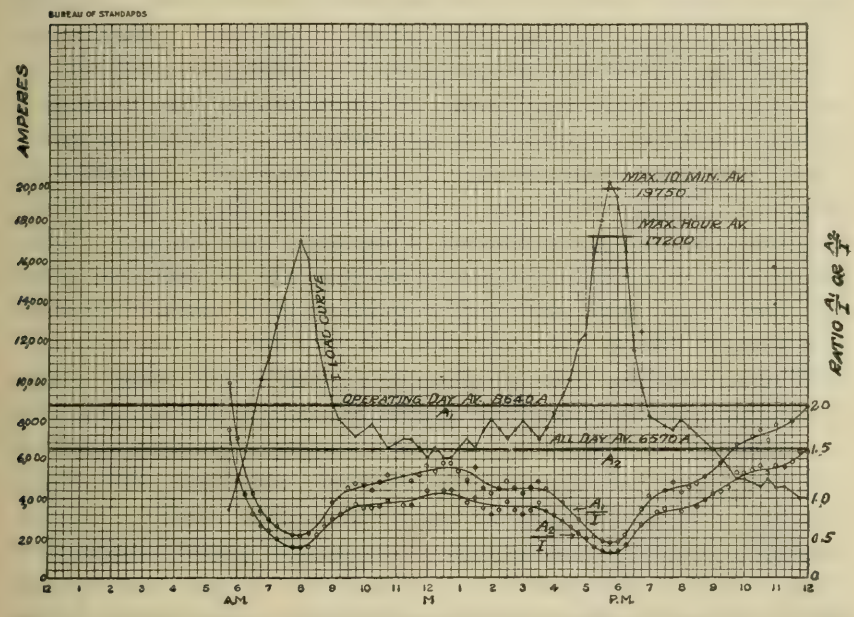

FIG. 17.—*Typical chart for correcting short-time readings to all-day or other average values*

eral, we would urge the taking of a large number of one-hour readings rather than a relatively small number of readings of a longer period, the one-hour readings being later reduced to average all-day values. The method of making this reduction is illustrated by curves in Fig. 17. In this figure curve *I* with the two high peaks is the load curve of a power station supplying a certain area under test. From this load curve either the operating-day average represented by the line A_1 can be determined, or the all-day or 24-hour average represented by the line A_2. If the reading at any point is taken during any particular hour of the day, its value reduced to the operating average would be the actual reading of the instrument multiplied by the ratio of the operating-

day average to the average ordinate of the load curve during the period when the reading was being taken. These ratios between the operating-day average and the actual value of the load are plotted in the curve marked $\frac{A_1}{I}$ and the ratios between the 24-hour average values and the actual load are plotted in the curve marked $\frac{A_2}{I}$. The ordinates of these curves for any hour can be used directly as the reduction factor to reduce an actual reading to an average for the day on either basis. For example, if the reading has been taken during the hour between 5 and 6 p. m., it will be very high, due to having been taken at practically the highest part of the load. By reference to the ratio curves it will be seen that to reduce this reading to the operating-day average it would have to be multiplied by substantially 0.5, while to reduce it to the 24-hour average value it would have to be multiplied by about ⅓. Load reduction curves of this sort should be prepared wherever a considerable number of readings are to be taken, after which the reduction of average readings for an hour or other relatively short time can readily be made to correspond to average all-day values.

When recording instruments are available we would recommend that readings always be taken covering a period of at least one-half hour, and preferably for one hour if time permits. Where, however, only indicating instruments are available and a large number of readings must be taken, short-time readings may be necessary, in which case accuracy must be sacrificed to expedition.

(*C*) **All-Day Average Basis.**—Where only a few readings are required, so that sufficient time can be given to the work, it is best to take all important readings over a period of a full day. In most cases, however, in making a complete electrolysis survey this can not be done, and readings have to be taken for a shorter period and reduced to the all-day values by the method described above.

III. EFFECT OF REVERSALS OF POLARITY

Throughout a large portion of every grounded railway return system it will be found that the potential differences between pipes and track frequently reverse in direction, the pipes becoming alternately positive and negative to earth with periods varying from a few seconds to several minutes or even longer; and special consideration has to be given to measurements in such places in

order that even an approximate estimate of their significance can be made. In general, four different classes of conditions have to be recognized in interpreting these measurements as follows:

(1) **Polarity of Pipes Always the Same.**—If the pipes are always of the same polarity, as, for example, always positive to surrounding structures, it is of course the arithmetical average value that should be used in judging the significance of the readings.

(2) **Polarity of Pipes Changing with Long Periods of Several Hours.**—If the pipes at any point are continuously positive for a period of several hours, and then of opposite polarity for a succeeding period of some hours, a condition which frequently exists in localities where a substation is operated during only a portion of the day, there will, in general, be very little protective effect due to the period when the pipe is negative to earth, and the actual corrosion is nearly indicated by the arithmetical average value of the voltage during the hours in which the pipe is positive to earth, this average of course being reduced to the 24-hour average basis. Thus, if a given pipe is found to be 4 volts positive to the tracks or other neighboring structure for a period of 12 hours, and either negative or at zero potential for the remaining 12 hours of the day, the actual amount of corrosion that would occur would undoubtedly be nearly equivalent to that which would result if the potential at the same point was maintained at 2 volts for the full 24 hours.

(3) **Polarity of Pipes Reversing with Periods of Only a Few Minutes.**—Under these conditions it has been shown by extensive experiments [7] that the corrosive process is in large measure reversible, and the actual amount of corrosion comes more nearly being proportional to the algebraic average of the applied potential than it is to the arithmetical average during the total time the pipe is positive. In all cases, therefore, where the polarity of the pipe is continuously reversing and the period of reversal does not exceed 5 or 10 minutes, the algebraic average should be used as the criterion of the importance of the reading.

(4) **Polarity of Pipes Reversing with Periods of from 15 Minutes to 1 Hour.**—Under these conditions neither the algebraic average nor the arithmetical average of the applied potential or current flow gives an accurate index of the amount of corrosion. For the shorter period the algebraic average comes more nearly being the best criterion, while as the period increases in length the arith-

[7] Technologic Paper No. 72, this Bureau.

metical average tends to give a better indication of the extent of the resulting corrosion. However, even where the period of reversal is as long as one hour the corrosive process is, under most conditions, to a considerable extent reversible and some allowance in interpreting the results should be made. The effect of the length of the period of reversal on corrosion is shown in the paper above referred to.

Part 5.—SELECTION OF INSTRUMENTS

In general, in making electrolysis surveys both indicating and recording instruments are required, the former being useful for taking very short-time readings of a preliminary nature that often assist materially in laying out a detailed plan for a comprehensive survey, and such instruments are also useful at times in certain kinds of measurements, such as measurements of current flow in large pipes where, because of the low value of the potential drop, recording instruments can not readily be obtained with sufficient sensitivity to record the values. Wherever it is practicable to use recording instruments, however, it is desirable to do so, since in this way readings can be taken over a greater length of time without unduly increasing the cost of the survey; and, moreover, a permanent record is obtained in which the personal element is eliminated.

On account of the variable and more or less irregular character of the readings, high accuracy in the measuring instruments is not required, but all instruments should be sufficiently rugged to yield moderate accuracy even under the severe handling such instruments must inevitably receive in field service.

In indicating instruments, which often have to be read quickly, owing to the highly variable character of the load, the scale should be so graduated that fractions of the numbered divisions can be quickly estimated without danger of error. This can be most easily and accurately done if the subdivisions are tenths of the numbered divisions. Since readings reverse frequently, zero-center instruments are usually desirable both in indicating and recording types. In many cases, especially in indicating instruments, it may be more convenient to have the zero a little to one side of the center so as to give a scale, such as -5, 0, $+10$ volts, or other ranges in the same proportion. This is desirable, owing to the fact that readings usually tend more strongly in one direction than in another, and in a scale of this kind a wider effective

range of the instrument is secured. For all purposes an instrument of very long period is desirable, since with rapidly fluctuating loads such an instrument can be more easily and accurately read, and it is the average values rather than momentary peaks that we desire to secure. When two instruments are to be read simultaneously it is important that they have identical periods, as otherwise phase displacements of the pointers may give rise to large errors. A long period is especially desirable in the case of recording instruments where, unless the period of the pointer be very long, the record will, on a rapidly fluctuating load, be so obscured that it will be practically impossible to determine the true average value of the reading over any desired period of time. We have frequently found it necessary to resort to special means to greatly increase the period of recording instruments. This has been done by shunting polarization cells of very large capacity around the moving coil of the instruments and having a certain amount of resistance in series with the instrument which, in many cases, can be the multiplier of the instrument. In this way periods of from 30 to 60 seconds have been obtained on Bristol recording instruments, and when such instruments are running on one-hour speed a smooth, distinct curve representing the algebraic average of the reading is obtained even with widely and rapidly fluctuating voltages. Although this result can be successfully achieved, the means for accomplishing it has not yet been developed beyond the experimental stage.

The volt sensitivity required of instruments is dependent on the range desired for each measurement, but it is often very important that the current sensitivity of the voltmeter should be high. High resistance is readily obtained in the better classes of instruments and should be sufficient to overshadow or permit an accurate correction for external resistance, such as long leads or soil contact resistance.

For an indicating instrument the Bureau of Standards has frequently used a special high-sensitivity voltmeter with a resistance of 2900 ohms per volt, and ranges of 5, 25, 50, and 100 volts have been found convenient and suitable for most voltage surveys in which an indicating instrument is needed. For recording instruments having a resistance of from 2 to 4 ohms in the lowest range, multipliers have been provided giving ranges of 0.005, 0.025, 0.1, 0.5, 2, 10, 50, and 150 volts. These ranges give a practically universal recording instrument for voltage and current survey work. The

lower ranges are used chiefly for current measurements by measuring the millivolt drop on a pipe or cable, the resistance of which is determined by calculation or from tables. Recording instruments for electrolysis work should always be of the dotting type, in order that they may have sufficient current sensitivity so that they may be given a high resistance in order to eliminate as far as practicable the necessity of correcting for the resistance of leads or contacts. Where such correction is found necessary it may conveniently be obtained by means of a very high resistance indicating instrument connected in parallel with the recorder. Where the necessary data are available the resistance of the circuit can be directly calculated, or in some cases it may be measured.

The Bureau of Standards has used in its survey work the Esterline dotting-type graphic recording voltmeter, and also the Bristol dotting-type smoke-chart recording voltmeter. Both of these instruments have been found very satisfactory for practically all purposes. The Esterline instrument has an advantage in certain cases, especially where readings are to be taken over a long period of time, because the ribbon-type record makes it practicable to run the chart at very high speed, and thus get greater detail over a long period without changing charts. Where records are to be taken over periods of one hour the Bristol instrument has some advantages. With this instrument running on the one-hour speed sufficient detail can be obtained for practically all purposes and the record at each point can be taken on a separate chart which greatly facilitates classification and filing of the records. The smoke-chart records have to be handled more carefully until after the record is taken and fixed, and this is in some cases a disadvantage. Figs. 18 and 19 show, respectively, typical Esterline and Bristol smoke-chart records.

For indicating instruments we have found several types of Weston instruments very satisfactory, and the Weston model 45, which can be had with double scale and in practically any range, is very much used. Keystone instruments made in triple ranges are also much used and are particularly useful where a very wide range of values must be taken with the fewest possible number of instruments.

For work requiring extremely high current sensitivity, such as for use with nonpolarizable electrodes, or for measuring extremely small potential drops on heavy metallic structures, a portable galvanometer is very desirable. An instrument which we have

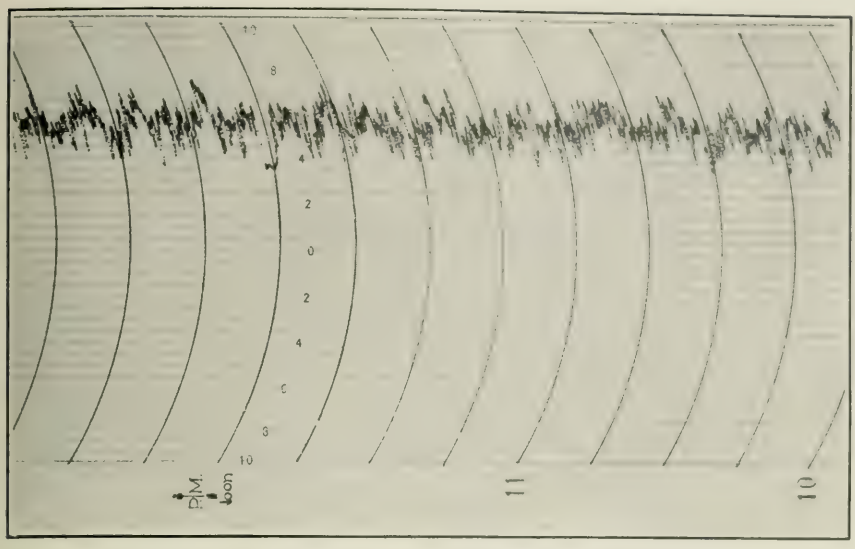

FIG. 18.—*Section of Esterline record*

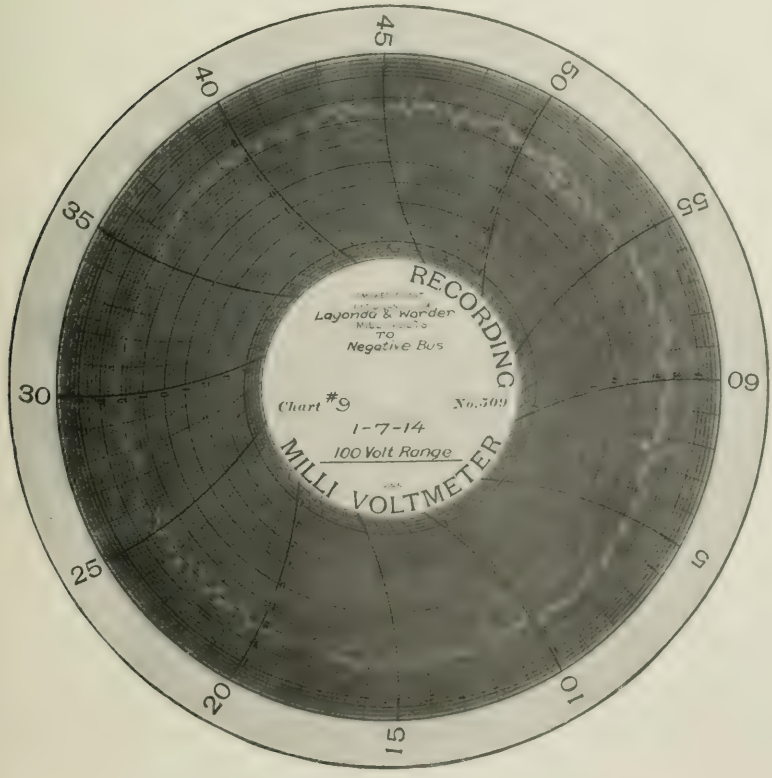

FIG. 19.—*Bristol smoke chart record*

used with much success for this work is a portable telescope galvanometer manufactured by Leeds & Northrup Co. The instruments of this type have a resistance of 225 ohms without multipliers, so that no special care need be exercised to secure very low resistance contacts on pipes such as is necessary with the ordinary millivoltmeters.

The telescope is mounted permanently with the instrument and the instrument possesses substantially the same degree of portability as ordinary portable voltmeters. In its use, however, considerably greater care is necessary in keeping the instrument level and we have found that the most convenient way to use it is to mount it on an ordinary surveyor's tripod. This not only facilitates leveling the instrument but brings it at an elevation where it can be conveniently read from a standing position. This instrument has a sensitivity of 20 megohms, and since its resistance is 225 ohms, as above stated, it would give a deflection of one scale division for about 1/88 of a millivolt.

For general electrolysis survey work we would recommend that one or more of all of the instruments mentioned above be available; and where very much work is to be done a considerable number of recorders will be found desirable both for reasons of economy and for expediting the tests.

Part 6.—NEED FOR SUPERVISION OF ELECTROLYSIS SURVEYS

It is well to emphasize here the desirability of having electrolysis surveys carried on under the direct supervision of a competent engineer thoroughly familiar with the subject of electrolysis from stray currents. The very great value of the properties generally exposed to possible danger from electrolysis is such as to make this question one of great importance. Further, the subject is a very complicated one, and not only are the sources of error in measurements and interpretation of results very great, but many of the measurements, unless studied and interpreted by one thoroughly familiar with the subject, may be so misleading as to destroy in large measure the value of the investigation.

While almost any one familiar with the use of electrical measuring instruments can carry out the details of the work, this should always be done under the supervision of an engineer who has had considerable experience in work of this kind, and where no local

engineer is available for supervising this work a competent consulting engineer should be employed. We can not too strongly urge upon the owners of underground utilities and railway companies the importance of considering this matter of electrolysis investigations in the light of a serious engineering problem and one which should not be dealt with by the more or less empirical and unscientific methods that have too often been followed in the past. It must be said, however, that there has in recent years been a marked tendency toward giving more careful and scientific study to this subject, and this has led to a marked betterment of electrolysis conditions in general throughout the country.

WASHINGTON, March 28, 1916.

APPENDIX—TABLES 1 AND 2

TABLE 1

Resistance and Other Data as to Pipes

Section A.—WROUGHT-IRON PIPE

Specimen No.	Card diameter (inches)	Weight (pounds per foot)		Variation from mean (per cent)	Specific gravity	Resistance			Variation from mean (per cent)
		Card	Observed			Microhms per foot	Microhms per pound-foot	Microhms per cubic centimeter	
B 1	0.25	0.42	0.387	− 7.8	.....	533.4	206.4	13.33	− 1.3
B 2	.25	.42	.411	− 2.1	7.579	477.9	196.4	12.56	− 6.1
B 3	.375	.56	.536	− 4.3	7.653	376.7	201.9	12.94	− 3.5
B 4	.375	.56	.546	− 2.5	.....	347.3	204.4	13.07	− 2.3
B 5	.50	.84	.858	+ 2.1	.....	234.5	201.2	12.81	− 3.8
B 6	.50	.84	.846	+ .7	7.549	232.0	196.3	12.58	− 6.2
B 7	.75	1.12	1.17	+ 3.5	.....	174.3	203.9	13.05	− 2.5
B 8	.75	1.12	1.11	− 1.8	7.615	185.0	205.3	13.18	− 1.9
B 9	1.00	1.67	1.76	+ 5.4	.....	115.9	204.0	13.09	− 2.5
B 10	1.00	1.67	1.74	+ 4.2	7.563	121.7	211.8	13.55	+ 1.2
B 11	1.25	2.25	2.23	− .9	7.670	87.08	193.7	12.09	− 7.4
B 12	1.25	2.25	2.21	− 1.8	.....	92.57	204.6	13.10	− 2.2
B 13	1.50	2.69	2.67	− .7	.....	72.66	194.0	12.42	− 7.3
B 14	1.50	2.69	2.82	+ 4.8	7.629	73.09	206.1	13.21	− 1.5
B 15	1.50	2.69	2.72	+ 1.1	.....	71.32	194.0	12.43	− 7.3
B 16	1.50	2.69	2.73	+ 1.5	.....	76.26	208.2	13.36	− .5
B 17	2.0	3.66	3.84	+ 4.9	7.659	50.35	193.3	12.39	− 7.6
B 18	2.0	3.66	3.71	+ 1.4	.....	52.24	193.8	12.45	− 7.4
B 19	2.5	5.77	5.86	+ 1.6	7.663	32.58	190.9	12.24	− 8.7
B 20	2.5	5.77	5.70	− 1.2	7.651	33.53	191.1	12.24	− 8.6
B 21	3.0	7.54	7.64	+ 1.3	.....	25.25	195.2	12.51	− 6.6
B 22	3.0	7.54	7.82	+ 3.7	.....	25.18	196.9	12.60	− 5.9
Y 1	3.75	.56	.494	−15.6	.....	424.1	209.6	13.44	+ .2
Y 2	.....	.....	.493	−12.0	.....	421.7	208.0	13.34	− .6
Y 3	.....	.....	.500	−10.7	7.578	413.4	206.8	13.26	− 1.1
Y 4	.50	.84	.821	− 2.3	.....	253.8	208.3	13.36	− .4
Y 5	.....	.....	.835	− .6	.....	251.1	209.6	13.44	+ .2
Y 6	.....	.....	.831	− 1.1	7.635	252.9	210.2	13.48	+ .5
Y 7	.75	1.12	1.13	− .9	.....	176.7	199.4	12.79	− 4.7
Y 8	.....	.....	1.12	0	.....	179.8	201.2	12.91	− 3.8
Y 9	.....	.....	1.12	0	7.643	179.2	201.5	12.92	− 3.7
Y 10	1.00	1.67	1.67	0	.....	119.8	200.2	12.84	− 4.3
Y 11	.....	.....	1.66	− .6	.....	119.3	198.5	12.73	− 5.1
Y 12	.....	.....	1.67	0	7.597	119.3	199.2	12.77	− 4.8
Y 13	1.25	2.25	2.30	+ 2.2	.....	90.42	208.2	13.35	− .5
Y 14	.....	.....	2.29	+ 1.8	.....	91.23	208.8	13.39	− .2
Y 15	.....	.....	2.29	+ 1.8	7.542	91.21	209.0	13.40	− .1
Y 16	1.50	2.69	2.64	− 1.9	.....	78.81	208.1	13.35	− .5
Y 17	.....	.....	2.65	− 1.5	.....	78.89	208.7	13.38	− .2
Y 18	.....	.....	2.68	− .4	7.608	77.67	208.1	13.34	− .5

TABLE 1—Continued

Resistance and Other Data as to Pipes—Continued

Section A.—WROUGHT-IRON PIPE—Continued

Specimen No.	Card diameter (inches)	Weight (pounds per foot)		Variation from mean (per cent)	Specific gravity	Resistance			Variation from mean (per cent)
		Card	Observed			Microhms per foot	Microhms per pound-foot	Microhms per cubic centimeter	
Y 19	2.00	3.66	3.48	− 4.9	.....	57.16	198.7	12.74	− 5.0
Y 20	.....	.....	3.46	− 5.5	.....	57.08	197.6	12.67	− 5.5
Y 21	.....	.....	3.51	− 4.1	7.582	56.32	197.6	12.67	− 5.5
Y 22	2.50	5.77	5.94	+ 2.9	.....	31.73	188.5	12.09	− 9.9
Y 23	.....	.....	5.94	+ 2.9	.....	32.49	191.7	12.37	− 8.4
Y 24	.....	.....	5.96	+ 3.3	7.671	32.70	194.9	12.50	− 6.8
Y 25	3.00	7.54	7.50	− .5	.....	26.09	195.7	12.55	− 6.5
Y 26	.....	.....	7.50	− .5	.....	26.49	198.7	12.74	− 5.0
Y 27	.....	.....	7.51	− .4	7.668	26.52	192.2	12.78	− 4.8
Y 28	3.50	9.05	8.72	− 3.6	.....	23.01	200.6	12.87	− 4.1
Y 29	4.00	10.72	10.6	− 1.1	.....	18.75	199.0	12.70	− 4.9
Y 30	4.50	12.49	12.9	+ 3.3	.....	15.61	201.9	12.95	− 3.5
Y 31	5.00	14.56	14.5	− .4	.....	14.14	205.7	13.19	− 1.7
Y 32	6.00	18.76	18.7	− .3	.....	10.61	198.1	12.71	− 5.3
R 1	.375	.56	.558	− .4	.....	416.2	232.1	15.00	10.9
R 2	.....	.....	.564	+ .7	.....	419.3	230.6	14.90	10.2
R 3	.....	.....	.572	+ 2.1	7.551	396.8	226.9	14.66	+ 8.5
R 4	.50	.84	.812	− 3.3	.....	265.9	216.0	13.95	+ 3.2
R 5	.....	.....	.815	− 3.0	.....	288.6	235.1	15.19	12.9
R 6	.....	.....	.817	− 2.7	7.509	265.9	217.2	14.03	3.8
R 7	.75	1.12	1.10	− 1.8	.....	216.5	238.3	15.40	13.9
R 8	.....	.....	1.10	− 1.8	.....	221.9	234.2	15.72	16.2
R 9	.....	.....	1.13	+ .9	7.441	206.0	233.7	15.10	11.2
R 10	1.0	1.67	1.68	+ .6	.....	127.2	213.0	13.76	+1.8
R 11	.....	.....	1.68	+ .6	.....	128.6	216.1	13.96	+3.3
R 12	.....	.....	1.67	0	7.589	124.5	208.4	13.46	− .08
R 13	1.25	2.25	2.25	0	.....	101.7	228.5	14.76	+9.2
R 14	.....	.....	2.28	+ 1.3	.....	106.4	242.0	15.64	15.7
R 15	.....	.....	2.32	+ 3.1	7.514	95.88	222.7	14.39	6.5
R 16	1.5	2.69	2.66	.....	.....	79.20	211.0	13.63	8.6
R 17	.....	.....	2.70	+ .4	.....	81.10	219.0	14.14	4.7
R 18	.....	.....	2.65	− 1.5	7.570	82.16	217.6	14.06	4.0
R 19	2.0	3.66	3.74	+ 2.2	.....	59.61	222.8	14.39	6.5
R 20	.....	.....	3.69	+ .8	.....	61.37	226.7	14.64	8.4
R 21	.....	.....	3.73	+ 1.9	7.584	60.08	224.5	14.47	7.3
R 22	2.5	5.77	5.87	+ 1.7	.....	37.10	217.7	14.06	3.4
R 23	.....	.....	5.86	+ 1.6	.....	37.37	219.0	14.15	4.7
R 24	.....	.....	5.84	+ 1.2	7.660	37.77	220.7	14.26	5.5
R 25	3.0	7.54	7.62	+ 1.1	.....	28.76	219.1	14.15	4.7
R 26	.....	.....	7.73	+ 2.5	.....	28.17	217.6	14.06	4.0
R 27	.....	.....	7.63	+ 1.2	7.602	28.58	218.0	14.09	4.2
R 28	3.5	9.05	8.90	− 1.7	.....	24.57	218.8	14.13	4.6
R 29	4.0	10.72	10.6	− 1.1	.....	20.27	215.4	13.91	3.0
R 30	4.5	12.49	12.6	− .9	.....	17.63	222.1	14.35	6.2
R 31	5.0	14.56	14.3	− 1.8	.....	14.99	214.4	13.85	2.5
R 32	6.0	18.76	18.4	− 1.9	.....	11.98	220.9	14.27	.....

TABLE 1—Continued

Resistance and Other Data as to Pipes—Continued

Section B.—STEEL PIPE, STANDARD WEIGHT

Specimen No.	Card diameter (inches)	Weight (pounds per foot)		Variation from mean (per cent)	Specific gravity	Resistance			Variation from mean (per cent)
		Card	Observed			Microhms per foot	Microhms per pound-foot	Microhms per cubic centimeter	
Y 33	0.25	0.42	0.420	0	.....	521.2	218.9	13.81	+1.4
Y 34	.25	.42	.425	+1.2	.....	517.4	219.9	13.87	+1.9
Y 35	.25	.42	.425	+1.2	.....	515.9	219.0	13.82	+1.4
Y 36	.375	.57	.556	−2.5	7.769	396.3	220.3	13.90	+2.0
Y 37	.375	.57	.556	−2.5	.....	403.9	224.7	14.17	+4.1
Y 38	.375	.57	.551	−3.3	.....	403.9	222.4	14.03	+3.0
Y 39	.50	.85	.796	6.5	7.754	261.6	208.2	13.13	−3.6
T 40	.50	.85	.799	−6.0	.....	261.1	208.7	13.16	−3.3
Y 41	.50	.85	.803	−5.5	.....	257.8	206.9	13.05	−4.2
Y 42	.75	1.13	1.11	−1.8	7.414	203.9	225.5	14.22	+4.4
Y 43	.75	1.13	1.10	−2.7	.....	206.5	227.1	14.33	+5.2
Y 44	.75	1.13	1.11	−1.8	.....	205.1	226.5	14.29	+4.9
Y 45	1.0	1.68	1.65	−1.8	7.706	132.3	218.3	13.77	+1.1
Y 46	1.0	1.68	1.64	−2.4	.....	133.0	217.5	13.72	+.7
Y 47	1.0	1.68	1.66	−1.2	.....	131.8	218.5	13.78	+1.2
Y 48	1.25	2.27	2.22	−2.2	7.739	98.44	218.1	13.76	+1.0
Y 49	1.25	2.27	2.22	−2.2	.....	98.41	218.2	13.76	+1.1
Y 50	1.25	2.27	2.22	−2.2	.....	97.91	217.1	13.68	+.6
Y 51	1.5	2.72	2.62	−3.7	7.804	84.84	222.2	14.02	+2.9
Y 52	1.5	2.72	2.62	−3.7	.....	84.43	221.5	13.97	+2.6
Y 53	1.5	2.72	2.62	−3.7	.....	84.78	222.4	14.03	+3.0
Y 54	2.0	3.65	3.44	−6.1	7.824	63.49	218.6	14.11	+1.3
Y 55	2.0	3.65	3.45	−5.8	.....	63.39	218.4	13.78	+1.2
Y 56	2.0	3.65	3.45	−5.8	.....	62.12	214.4	13.52	−.7
Y 57	2.5	5.79	5.88	+1.6	7.815	37.96	223.3	14.09	+3.4
Y 58	2.5	5.79	5.90	+1.9	.....	37.11	218.8	13.80	+1.3
Y 59	2.5	5.79	5.88	+1.6	.....	37.33	219.6	13.85	+1.7
Y 60	3.0	7.58	7.64	+.8	7.843	28.02	214.0	13.50	−.9
Y 61	3.0	7.58	7.62	+.5	.....	28.14	214.5	13.53	−.6
Y 62	3.0	7.58	7.65	+.9	.....	28.20	215.7	13.61	.1
Y 63	3.5	9.11	9.02	−1.0	.....	23.93	215.8	13.62	0
Y 64	5.0	14.62	13.09	−4.9	.....	15.83	219.9	13.87	+1.9
Y 65	6.0	18.97	17.9	−5.6	.....	12.07	216.6	13.66	+.3
N 23	.....	.....	2.46	.....	.....	85.0	209	13.07	−3.2
N 24	.....	.....	2.47	.....	.....	85.1	210	13.14	−2.7
N 25	.....	.....	2.47	.....	.....	84.2	208	12.98	−3.7
N 26	.....	.....	2.47	.....	7.83	84.8	209	13.08	−3.2
N 27	.....	.....	2.49	.....	.....	83.0	207	12.90	−4.1
N 28	1.25	2.27	2.17	−4.4	.....	95.8	208	12.98	−3.7
N 29	1.25	2.27	2.17	−4.4	7.79	96.4	209	13.09	−3.2
N 30	1.25	2.27	2.15	−5.3	.....	97.3	209	13.11	−3.2
N 31	.75	1.13	1.13	0	7.80	183.8	208	12.99	−3.7
N 32	.75	1.13	1.14	+.9	.....	186.6	213	13.25	−1.3
N 33	.75	1.13	1.14	+.9	.....	184.6	210	13.18	−2.7
N 34	.375	.57	.56	−1.8	7.76	399.0	223	13.86	+3.2
N 35	.375	.57	.56	−1.8	.....	394.0	221	13.92	+2.7
N 36	.375	.57	.57	0	.....	389.0	222	13.83	+2.8

TABLE 1—Continued

Resistance and Other Data as to Pipes—Continued

Section B.—STEEL PIPE, STANDARD WEIGHT—Continued

Specimen No.	Card diameter (inches)	Weight (pounds per foot)		Variation from mean (per cent)	Specific gravity	Resistance			Variation from mean (per cent)
		Card	Observed			Microhms per foot	Microhms per pound-foot	Microhms per cubic centimeter	
N 37	.125	.24	.24	0	.....	934.0	224	13.77	+3.8
N 38	.125	.24	.23	−4.2	7.82	928.0	214	13.34	− .9
N 39	.125	.24	.23	−4.2	.....	926.0	213	13.45	−2.9
N 40	2.0	3.65	3.44	−6.0	.....	60.8	209	13.07	−3.2
N 41	2.0	3.65	3.45	−5.6	7.83	60.6	209	13.05	−3.2
N 42	2.0	3.65	3.48	−4.7	.....	60.2	209	13.07	−3.2
N 43	.....	.....	3.92	.....	.....	52.4	205	12.85	−5.1
N 44	.....	.....	3.84	.....	7.83	56.4	216	13.54	0
N 45	.....	.....	3.83	.....	.....	57.0	218	13.65	+1.0
N 46	.....	.....	3.92	.....	.....	52.6	206	12.91	−4.6
N 47	.....	.....	3.83	.....	.....	57.0	218	13.64	+1.0
N 48	3.5	9.11	10.18	.....	.....	20.9	213	13.29	−1.3
N 49	3.5	9.11	10.23	.....	.....	20.9	213	13.35	−1.3
N 50	3.5	9.11	10.23	.....	.....	20.8	212	13.29	−1.8
N 51	6.0	18.97	18.33	−3.4	.....	11.87	218	13.60	−1.0
N 52	6.0	18.97	18.38	−3.1	.....	11.81	217	13.56	+ .5
N 53	6.0	18.97	18.37	−3.2	.....	11.96	221	13.72	+2.4
Average	.....	.....	.....	2.3	.....	.....	215.8	13.56	2.3

Section C.—CAST-IRON PIPE, CLASS B

100	3.0	14.6	13.8	− 5.5	6.803	93.24	1287	89.48	+ 4.9
101	3.0	14.6	14.2	− 2.7	7.086	88.73	1259	85.58	+ 2.6
102	4.0	20.06	16.8	−16.2	7.070	72.09	1211	83.81	− 1.3
103	4.0	20.06	17.0	−15.2	7.056	73.17	1244	85.81	+ 1.4
104	6.0	31.14	27.5	−11.6	7.033	39.05	1074	74.15	−12.5
105	6.0	31.14	30.8	− 1.1	7.035	44.05	1357	93.85	+10.6
200	4.0	20.06	18.3	− 8.7	7.000	65.40	1198	82.71	− 2.4
201	4.0	20.06	16.8	−16.2	7.044	69.05	1160	80.32	− 5.5
202	4.0	20.06	18.0	−10.2	6.980	65.91	1186	81.90	− 3.3
203	4.0	20.06	17.3	−13.7	7.030	68.31	1182	81.75	− 3.7
204	4.0	20.06	20.7	+ 3.2	7.106	49.73	1029	71.35	−16.1
205	4.0	20.06	20.7	+ 3.2	7.087	55.04	1139	78.94	− 7.2
300	6.0	31.14	27.4	−12.0	7.102	38.25	1048	72.44	−14.6
301	6.0	31.14	28.4	− 7.8	7.085	38.59	1096	75.67	−10.7
302	6.0	31.14	27.8	−10.7	7.117	38.26	1063	73.42	−13.0
303	6.0	31.14	28.3	− 9.1	7.084	38.22	1082	74.64	−11.8
400	4.0	20.06	18.6	− 7.3	7.188	75.06	1396	96.75	+13.8
401	4.0	20.06	17.7	−11.7	7.019	74.84	1325	91.52	+ 8.0
402	4.0	20.06	19.0	− 5.3	7.227	69.60	1322	91.43	+ 7.9
500	6.0	31.14	27.8	−10.7	7.096	54.15	1505	104.1	+22.7
501	6.0	31.14	28.2	+ 9.4	7.065	51.10	1441	99.71	+17.4
502	6.0	31.14	28.2	+ 9.4	7.037	49.18	1387	95.79	+13.0
Average	.....	.....	.....	9.1	.....	.....	1227	84.83	9.3

TABLE 1—Continued

Resistance and Other Data as to Pipes—Continued

Section D.—INGOT IRON PIPE

Specimen No.	Card diameter (inches)	Weight (pounds per foot)		Variation from mean (per cent)	Specific gravity	Resistance			Variation from mean (per cent)
		Card	Observed			Microhms per foot	Microhms per pound-foot	Microhms per cubic centimeter	
A 1	2.0	Not standard	3.81	Not standard	.....	46.03	175.2	10.90	−1.2
A 2	2.0		3.83		.....	46.31	177.2	11.02	− .1
A 3	2.0		3.80		7.858	46.65	177.4	11.04	+ .1
A 4	2.5		4.66		.....	38.20	178.1	11.08	+ .4
A 5	2.5		4.69		.....	37.98	178.2	11.08	+ .5
A 6	2.5		4.71		7.837	37.69	177.7	11.05	+ .2
A 7	3.0		6.07		.....	29.54	179.2	11.14	+1.0
A 8	3.0		6.08		.....	29.20	177.6	11.05	+ .2
A 9	3.0		6.14		7.858	29.02	178.2	11.08	+ .5
A 10	3.5		6.61		.....	26.95	178.2	11.08	+ .5
A 11	3.5		6.64		.....	26.70	177.3	11.03	.....
A 12	3.5		6.63		.....	26.41	175.1	10.89	−1.3
A 13	4.5		12.28		.....	14.41	177.0	11.01	− .2
Average	.....	.....	.....	.....	7.851	.....	177.3	11.03	.5

Section E.—COPPER STEEL PIPE

11 [a]	2.0	Not standard	3.38	Not standard	7.810	78.4	265	16.57	+0.1
12 [a]	2.0		3.37		7.817	78.7	265	16.55	− .1
13 [a]	2.0		3.39		7.827	78.4	266	16.57	+ .1
21 [b]	1.5		2.48		7.819	94.9	236	14.71	+ .2
22 [b]	1.5		2.50		7.822	94.2	236	14.72	+ .3
23 [b]	1.5		2.52		7.809	93.0	234	14.62	− .4
31 [c]	2.0		3.53		7.845	61.3	217	13.45	+ .4
32 [c]	2.0		3.53		7.851	60.7	214	13.33	− .5
33 [c]	2.0		3.53		7.830	61.0	215	13.42	+ .1
41 [d]	2.0		3.45		7.861	72.0	248	15.42	+ .8
42 [d]	2.0		3.61		7.869	68.3	246	15.30	0
43 [d]	2.0		3.73		7.856	65.5	244	15.17	− .8

[a] Bessemer steel 1.00 per cent.
[b] Bessemer steel 0.35 per cent.
[c] Open-hearth steel 0.20 per cent.
[d] Seamless steel 3.25 per cent.

TABLE 1—Continued

Resistance and Other Data as to Pipes—Continued

Section F.—LEAD PIPE

Specimen No.	Card diameter (inches)	Weight (pounds per foot)		Variation from mean (per cent)	Specific gravity	Resistance			Variation from mean (per cent)
		Card	Observed			Microhms per foot	Microhms per pound-foot	Microhms per cubic centimeter	
L 1	0.25 (8 oz.)	0.5	0.456	− 8.8	.....	1093	499.0	21.45	+1.5
L 2	.25	.5	.456	− 8.8	.....	1101	501.9	21.57	+2.1
L 3	.25	.5	.459	− 8.2	.....	1062	487.6	20.96	− .8
L 4	.75 (AA)	3.5	3.564	+ 1.8	.....	137.8	491.1	21.11	− .1
L 5	.75 (AA)	3.5	3.576	+ 2.2	.....	136.4	487.9	20.93	− .7
L 6	.75 (AA)	3.5	3.576	+ 2.2	.....	136.9	489.5	21.05	− .4
L 7	.75 (AA)	3.5	3.495	− .1	.....	140.4	490.6	21.12	− .2
L 8	.75 (AA)	3.5	3.480	− .6	.....	139.9	486.9	20.92	− .9
L 9	.75 (AA)	3.5	3.477	− .7	.....	141.5	491.8	21.13	+ .1
L 10	1.00 (c)	2.5	2.419	− 3.3	.....	203.5	492.2	21.16	+ .1
L 11	1.00 (c)	2.5	2.422	− 3.1	.....	203.2	492.2	21.13	+ .1
L 12	1.00 (c)	2.5	2.429	− 2.8	.....	201.7	490.0	21.08	− .3
L 13	1.00 (AA)	4.75	4.766	+ .3	.....	102.2	487.0	20.92	− .9
L 14	1.00 (AA)	4.75	4.766	+ .3	.....	101.7	484.5	20.87	−1.4
L 15	1.00 (AA)	4.75	4.762	+ .3	.....	102.4	487.5	20.97	− .4
L 16	2.00 (c)	6.0	5.768	− 3.9	.....	84.70	488.6	21.00	− .6
L 17	2.00 (c)	6.0	5.772	− 3.8	.....	85.09	491.2	21.10	− .1
L 18	2.00 (c)	6.0	5.781	− 3.6	.....	84.94	491.3	21.12	.0
L 19	2.00 (AA)	9.0	8.888	− 1.2	.....	55.13	490.0	21.08	− .3
L 20	2.00 (AA)	9.0	8.926	− .8	.....	55.21	492.8	21.18	+ .3
L 21	2.00 (AA)	9.0	8.939	− .7	.....	55.23	493.7	21.20	+ .4
L 22	.25 (8 oz.)	.5	.452	− 9.6	.....	1093.0	493.6	21.21	+ .4
L 23	.25 (8 oz.)	.5	.449	−10.2	.....	1095.0	491.4	21.12	.0
L 24	.25 (8 oz.)	.5	.452	− 9.6	.....	1093.0	494.2	21.23	+ .6
L 25	.75 (c)	1.75	1.640	− 6.3	.....	302.8	496.7	21.32	+1.1
L 26	.75 (c)	1.75	1.650	− 5.7	.....	299.1	493.5	21.20	+ .4
L 27	.75 (c)	1.75	1.639	− 6.3	.....	301.0	493.2	21.20	+ .3
Average	.....	.....	.....	3.9	.....	.....	491.5	21.12	0.5

TABLE 2

Resistance and Current Data for Pipes

CAST-IRON PIPE

Nominal inside diameter (inches)	Weight (pounds per foot)	Resistance (microhms per foot)	Current for 1 mv on 1 foot (amperes)	Weight (pounds per foot)	Resistance (microhms per foot)	Current for 1 mv on 1 foot (amperes)
	A. W. W. A. standard, Class A			A. W. W. A. standard, Class B		
3	13.04	94.0	10.6	14.6	84.0	11.9
4	18.03	68.0	14.7	20.06	61.0	16.4
6	27.90	44.0	22.7	31.14	39.4	25.4
8	38.74	31.7	31.6	42.68	28.8	34.8
10	51.95	23.6	42.3	58.80	20.9	47.9
12	66.90	18.3	55.0	76.44	16.1	62.0
14	82.33	14.9	67.0	94.82	12.9	77.0
16	98.75	12.4	81.0	114.7	10.7	94.0
18	118.1	10.4	96.0	137.7	8.9	112.0
20	137.2	8.9	112.0	163.2	7.5	133.0
24	186.5	6.5	152.0	217.1	5.7	177.0
30	265.1	4.63	216.0	312.6	3.93	255.0
36	357.8	3.43	292.0	419.0	2.93	342.0
42	465.6	2.64	379.0	541.5	2.27	441.0
48	607.7	2.02	495.0	688.5	1.78	560.0
54	730.2	1.68	600.0	842.8	1.46	690.0
60	835.6	1.47	680.0	1012.0	1.21	820.0
72	1169.0	1.05	950.0	1416.0	.87	1150.0
84	1441.0	.85	1170.0	1860.0	.66	1520.0
	A. W. W. A. standard, Class C			A. W. W. A. standard, Class D		
3	15.47	79.0	12.6	16.37	75.0	13.3
4	21.27	58.0	17.3	22.83	54.0	18.6
6	32.93	37.3	26.8	35.30	34.8	28.8
8	47.97	25.6	39.1	51.16	24.0	41.7
10	65.66	18.7	54.0	71.54	17.2	58.0
12	85.26	14.4	70.0	93.59	13.1	76.0
14	108.0	11.4	88.0	119.1	10.3	97.0
16	133.3	9.2	109.0	147.5	8.3	120.0
18	162.4	7.6	132.0	178.4	6.9	145.0
20	190.9	6.4	156.0	212.4	5.8	173.0
24	257.7	4.76	210.0	286.2	4.29	233.0
30	367.5	3.34	300.0	421.4	2.91	343.0
36	499.8	2.46	407.0	580.7	2.11	473.0
42	656.6	1.87	540.0	762.0	1.61	620.0
48	833.0	1.47	680.0	960.4	1.28	780.0
54	1041.0	1.18	850.0	1227.0	1.0	1000.0
60	1220.0	1.01	990.0	1458.0	.84	1190.0
72	1744.0	.70	1420.0			

38592°—16——6

TABLE 2—Continued

Resistance and Current Data for Pipes—Continued

CAST-IRON PIPE—Continued

Nominal inside diameter (inches)	Weight (pounds per foot)	Resistance (microhms per foot)	Current for 1 mv on 1 foot (amperes)	Weight (pounds per foot)	Resistance (microhms per foot)	Current for 1 mv on 1 foot (amperes)
	New England W. W. A. standard,[a] Class A			New England W. W. A. standard,[a] Class B		
4	14.89	82.0	12.1			
6	24.32	50.0	19.8			
8	35.58	34.5	29.0			
10	49.04	25.0	40.0	52.03	23.6	42.4
12	61.14	20.1	50.0	65.92	18.6	54.0
14	76.85	15.9	63.0	82.41	14.9	67.0
16	90.98	13.5	74.0	98.95	12.4	81.0
18	104.5	11.7	85.0	115.2	10.6	94.0
20	121.9	10.1	99.0	133.7	9.2	109.0
24	155.6	7.9	127.0	174.4	7.0	142.0
30	215.3	5.7	176.0	244.8	5.0	200.0
36	287.0	4.27	234.0	326.0	3.76	266.0
42	368.4	3.33	300.0	422.1	2.91	344.0
48	459.3	2.67	374.0	350.2	2.31	432.0
54	559.8	2.19	456.0	650.3	1.89	530.0
60	664.0	1.85	540.0	782.3	1.57	640.0
	New England W. W. A. standard,[a] Class C			New England W. W. A. standard,[a] Class D		
4	15.7	78.0	12.8			
6	26.72	45.9	21.8			
8	40.38	30.4	32.9			
10	54.99	22.3	444.8	57.94	21.2	47.2
12	70.67	17.4	58.0	75.39	16.3	61.0
14	87.97	14.0	72.0	94.85	12.9	77.0
16	106.9	11.5	87.0	114.8	10.7	93.0
18	127.4	9.6	104.0	138.0	8.9	112.0
20	147.6	8.3	120.0	161.4	7.6	132.0
24	196.3	6.2	160.0	215.3	5.7	175.0
30	277.7	4.42	226.0	307.3	3.99	250.0
36	373.3	3.29	304.0	412.3	2.97	336.0
42	481.1	2.55	392.0	538.9	2.28	439.0
48	608.0	2.02	495.0	678.9	1.81	550.0
54	749.5	1.64	610.0	839.9	1.46	680.0
60	911.5	1.35	740.0	1029.7	1.19	840.0
	A. G. I. standard gas					
4	17.3	71.0	14.1			
6	27.3	45.0	22.2			
8	38.0	32.3	30.9			
10	51.0	24.1	41.5			
12	67.0	18.3	55.0			
16	102.0	12.0	83.0			
20	139.0	8.8	113.0			
24	186.0	6.6	152.0			
30	256.0	4.79	209.0			
36	346.0	3.55	282.0			
42	453.0	2.71	369.0			
48	610.0	2.02	495.0			

[a] Specific resistance = 1227. Microhms per pound-foot.

TABLE 2—Continued

Resistance and Current Data for Pipes—Continued

STEEL PIPE [a]

Nominal inside diameter (inches)	Weight (pounds per foot)	Resistance (microhms per foot)	Current for 1 mv on 1 foot (amperes)	Weight (pounds per foot)	Resistance (microhms per foot)	Current for 1 mv on 1 foot (amperes)
	Standard			Extra strong		
0.125	0.24	900.0	1.11	0.31	700.0	1.44
0.25	.42	510.0	1.95	.54	400.0	2.50
0.375	.57	379.0	2.64	.74	292.0	3.43
0.50	.85	254.0	3.94	1.09	198.0	5.0
0.75	1.13	191.0	5.2	1.47	147.0	6.8
1	1.68	129.0	7.8	2.17	100.0	10.1
1.25	2.27	95.0	10.5	3.00	72.0	13.9
1.50	2.72	79.0	12.6	3.63	60.0	16.8
2	3.65	59.0	16.9	5.02	43.0	23.3
2.50	5.79	37.3	26.8	7.66	28.2	35.5
3	7.58	28.5	35.1	10.25	21.1	47.5
3.50	9.11	23.7	42.2	12.51	17.3	58.0
4	10.79	20.0	50.0	14.98	14.4	69.0
4.50	12.54	17.2	58.0	17.61	12.3	82.0
5	14.62	14.8	68.0	20.78	10.4	96.0
6	18.97	11.4	88.0	28.57	7.6	132.0
7	23.54	9.2	109.0	38.05	5.7	176.0
8	24.70	8.7	114.0	43.39	4.98	201.0
8	28.55	7.6	132.0	.....	.....	.....
9	33.91	6.4	157.0	48.73	4.43	226.0
10	31.20	6.9	145.0	54.74	3.94	254.0
10	34.24	6.3	159.0	.....	.....	.....
10	40.48	5.3	188.0	.....	.....	.....
11	45.56	4.74	211.0	60.08	3.59	278.0
12	43.77	4.93	203.0	65.42	3.30	303.0
12	49.56	4.36	230.0	.....	.....	.....
13	54.57	3.96	253.0	72.09	3.00	334.0
14	58.57	3.69	271.0	77.43	2.79	359.0
15	62.58	3.45	290.0	82.77	2.61	383.0

WROUGHT-IRON PIPE [b]

0.125	0.24	870.0	1.15	0.29	720.0	1.39
0.25	.42	498.0	2.01	.54	387.0	2.58
0.375	.56	374.0	2.68	.74	283.0	3.54
0.50	.84	249.0	4.02	1.09	192.0	5.2
0.75	1.12	187.0	5.4	1.39	150.0	6.6
1.0	1.67	125.0	8.0	2.17	96.0	10.4
1.25	2.25	93.0	10.8	3.00	70.0	14.3
1.50	2.69	78.0	12.9	3.63	58.0	17.4
2.0	3.66	57.0	17.5	5.02	41.7	24.0
2.50	5.77	36.3	27.6	7.67	27.3	36.7
3.0	7.54	27.8	36.0	10.25	20.4	49.0
3.50	9.05	23.1	43.3	12.47	16.8	60.0
4.0	10.72	19.5	51.0	14.97	14.0	72.0
4.50	12.49	16.8	60.0	18.22	11.5	87.0

[a] National Tube Co. tables, 1913. Specific resistance=215.8 microhms per pound-foot.
[b] Byers' table of weights. Specific resistance=209.3 microhms per pound-foot.

TABLE 2—Continued

Resistance and Current Data for Pipes—Continued

WROUGHT-IRON PIPE—Continued

Nominal inside diameter (inches)	Weight (pounds per foot)	Resistance (microhms per foot)	Current for 1 mv on 1 foot (amperes)	Weight (pounds per foot)	Resistance (microhms per foot)	Current for 1 mv on 1 foot (amperes)
5.0	14.56	14.4	70.0	20.54	10.2	98.0
6.0	18.76	11.2	90.0	28.58	7.3	137.0
7.0	23.41	8.9	112.0	37.67	5.6	180.0
8.0	25.00	8.4	120.0	43.00	4.87	206.0
8.0	28.34	7.4	136.0			
9.0	33.70	6.2	161.0	48.73	4.29	233.0
10.0	32.00	6.5	153.0			
10.0	35.00	6.0	167.0			
10.0	40.00	5.2	191.0	54.74	3.82	262.0
11.0	45.00	4.70	215.0	60.08	3.48	287.0
12.0	45.00	4.70	215.0			
12.0	49.00	4.27	234.0	65.42	3.20	313.0

LEAD PIPE

Specimen No.	Card diameter (inches)	Card weight (pounds per foot)	Resistance (microhms per foot)	Current for 1 mv drop per foot (amperes)
1	0.25	0.5	1093.0	0.915
2	.25	.5	1101.0	.908
3	.25	.5	1062.0	.942
4	.75 (AA)	3.5	137.8	7.257
5	.75 (AA)	3.5	136.4	7.332
6	.75 (AA)	3.5	136.9	7.305
7	.75 (AA)	3.5	140.4	7.123
8	.75 (AA)	3.5	139.9	7.148
9	.75 (AA)	3.5	141.5	7.067
10	1.00 (C)	2.5	203.5	4.914
11	1.00 (C)	2.5	203.2	4.921
12	1.00 (C)	2.5	201.7	4.958
13	1.00 (AA)	4.75	102.2	9.785
14	1.00 (AA)	4.75	101.7	9.833
15	1.00 (AA)	4.75	102.4	9.766
16	2.00 (C)	6.0	84.70	11.81
17	2.00 (C)	6.0	85.09	11.78
18	2.00 (C)	6.0	84.94	11.77
19	2.00 (AA)	9.0	55.13	18.14
20	2.00 (AA)	9.0	55.21	18.11
21	2.00 (AA)	9.0	55.23	18.11
22	.25	.5	1093.0	.915
23	.25	.5	1095.0	.913
24	.25	.5	1093.0	.915
25	.75 (C)	1.75	302.8	3.301
26	.75 (C)	1.75	299.1	3.343
27	.75 (C)	1.75	301.0	3.322

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S. W. STRATTON, DIRECTOR

No. 29

VARIATIONS IN RESULTS OF SIEVING WITH STANDARD CEMENT SIEVES

BY

RUDOLPH J. WIG

and

J. C. PEARSON

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By Rudolph J. Wig and J. C. Pearson

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I. INTRODUCTION

Since the development of the Bureau's specification for standard cement sieves [1] inquiries have been received as to the limits of accuracy of sieves measured and sealed by the Bureau as standard sieves, when they are used in the laboratory in determining the degree of fineness of a sample of cement or other material.

As the degree of fineness is usually made a part of the specification and contract upon which the cement is purchased and the material may be rejected if the fineness falls below a certain requirement, the accuracy of the fineness determination is often in dispute, and there is no available information as to the tolerance which should be placed upon such determinations.

The testing of sieves and sieve cloth by the Bureau during the past two years has shown that the tolerance of the present specification for diameter of wire and spacing can not be much reduced without making the cost of such selected cloth prohibitive.

A number of tests have recently been carried out at the Bureau of Standards to see what order of discrepancy may be expected in fineness determinations of cement when made by the standard routine method of sieving.

10646°—13

[1] Circular No. 39, Bureau of Standards.

II. SCOPE OF TESTS

Discrepancies in determinations of fineness may be attributed to: (*a*) Differences in the standard sieves; (*b*) the "personal equation" of the observer; (*c*) lack of uniformity in the samples; (*d*) the residual differences when the three foregoing sources of error are, as far as possible, eliminated.

Considering the last mentioned first, it is evident that the experienced and careful worker, using a high-grade sieve and sieving samples of a well-dried and thoroughly mixed cement according to a fixed program, can by repeated trials determine a maximum limit of tolerance for residual differences. When this has been established, the same observer is in a position to check uniformity of samples of other cements—that is, he may check their uniformity only with an accuracy not greater than his own maximum limit of tolerance. There is at present, so far as we know, no simpler method of detecting lack of uniformity in finely ground material.

Following the results reported below, an attempt has been made to establish—

1. What variations in fineness determinations are permissible under the most favorable conditions.

2. What variations may arise from differences in the "standard" sieves themselves.

3. What error may be looked for in a single fineness determination on a standard sieve as performed by an ordinary laboratory worker of average experience.

4. Whether variations from the standard method of sieving are appreciable.

5. Whether "personal equation" is appreciable in the limited number of tests made.

6. Whether an arbitrary system of "demerits" determined from careful measurements of a sieve is a reliable indication of its sieving value.

III. TESTS

The tests were made on a lot of sieves submitted for the purpose by two well-known firms. As indicated below, four men made independent determinations of fineness on 24 of the sieves, while two men made the majority of determinations on the remaining sieves. The cement used was a good brand of normal grade Portland, which was first thoroughly dried, screened through a No. 20 sieve, and finally mixed by long-continued rolling on a large sheet of stout manila wrapping paper. The determinations were made according to the standard method of sieving described in the United States Government Specification for Portland Cement,[1] as follows:

> The determination of fineness should be made on a 50-gram sample, which may be dried at a temperature of 100° C (212° F) prior to sifting. The coarsely-screened sample (cement is ordinarily screened through a No. 20 sieve before mixing for routine tests) should be weighed and placed on the No. 200 sieve, which, with the pan and cover attached, should be held in one hand in a slightly inclined position and moved forward and backward in the plane of inclination, at the same time striking the side gently about two hundred times per minute against the palm of the other hand on the upstroke. The operation is to be continued until not more than 0.05 grams will pass through in one minute.

While the experienced worker always develops some peculiarity in his method of sifting, which contributes to or determines his "personal equation," undoubtedly the chief factor to be guarded against is carelessness. This factor may explain to some extent the rather wide variations observed, but it may be safely assumed that the sum total of carelessness on the part of those who participated in the tests is less, rather than greater, than that made in normal routine work, and it is believed that the average results represent what may be expected from experienced routine workers in similar laboratories.

[1] Circular No. 33, Bureau of Standards.

In the following tables the observers are designated by letters and the sieves by numbers:

TABLE 1

Results of Sieving Tests Made by Four Observers on 12 Standard No. 200 Sieves

Sieve	Observers					Average	Maximum variation from average
	A	B	C	D	E		
1	80.30	79.72	80.40	80.24		80.16	0.44
2	79.88	80.66	80.20	80.46		80.30	.42
3	79.78	80.44	80.44 80.44		80.51	80.32	.54
4	80.62	80.00	80.44	80.76		80.46	.46
5	80.50	80.72	80.18	80.56		80.49	.31
6	80.24	80.84	80.66	80.36		80.52	.32
7	80.40	80.57	80.44	80.80		80.55	.25
8	80.30	80.82	80.26	81.14		80.63	.51
9	80.34	80.90	80.72	81.04		80.75	.41
10	80.56	80.76	80.90	81.50		80.93	.57
11	80.42	80.40	81.36	81.60		80.94	.66
12	81.04	81.00	80.76	81.34		81.03	.31
Average	80.36	80.57	80.55	80.89		80.59	.43
Personal equation	+.23	+.02	+.04	−.29			

Table 1 shows the results obtained by four observers using the same cement on 12 standard No. 200 sieves. The figures are percentages of total cement passing the sieves.

An approximate value of the range that may be expected due to differences in the sieves may be obtained from the averages for each sieve, which are taken as the most probable sieving values. The highest is seen to be 81.03 per cent, the lowest 80.16 per cent, range 0.87 per cent. A "standard" sieve according to these results, may therefore differ from the mean value of a number of good sieves by nearly 0.5 per cent. It is to be borne in mind, however, that the mean value of a number of good sieves will generally be greater than the amount passed by an ideal No. 200 sieve, since the prescribed limits of tolerance allow greater latitude below 200 meshes than above. Thus, careful measurements of cloth on sieve No. 1 showed this to be the nearest of the

lot to the ideal No. 200 sieve, and repeated fineness determinations with this sieve showed that its most probable sieving value was about 80.30 per cent, which is 0.3 per cent less than the observed average value for all the sieves. It follows, therefore, that a "standard" sieve may have a true correction to the ideal sieve of as much as 0.7 per cent.

The last column of Table 1 shows that the error to be looked for in a single fineness determination is likely to be at least 0.5 per cent, a figure which will, of course, vary with the reliability of the observer. A search through Table 1, however, will show that all the observers have missed the average value on one or more sieves by more than 0.4 per cent.

A roughly approximate value of personal equation may be obtained by averaging all the determinations made by each observer and comparing this with the mean value of all observers. The values are given in the last line of Table 1. The number of observers is too small to establish this factor with any certainty, but for observers A and D, whose averages show appreciable deviations from the others, it may be noted that 8 times out of 12 A's value is less than the mean value for the sieves, and 8 times out of 12 D's value is greater than the mean value for the sieves.

TABLE 2

Results of Sieving Tests Made by One Observer on 1 Standard Sieve using Five Different Methods

Trial	1 (200 strokes)	2 (250 strokes)	3 (150 strokes)	4 (Single washer)	5 (6 steel balls)
1	80.30	80.06	80.44	79.76	80.36
2	80.44	80.08	80.36	79.46	79.98
3	80.16	80.02	80.24	80.08	80.18
Average	80.30	80.05	80.35	79.77	80.17

Table 2 represents the results obtained by a single observer on sieve No. 1, using five slightly varying methods of sieving, each method being given three careful trials. These methods include the deviations from the standard method of sieving which are

sometimes permitted in fineness determinations. Column 1 contains the results obtained by moving the sieve back and forth 200 times per minute, that is, according to the standard specifications. Column 2 contains the results obtained from sieving at the rate of 250 strokes per minute, this rate requiring, of course, short quick strokes. Similarly Column 3 contains the results obtained by sieving at the rate of 150 strokes per minute, the strokes being relatively long and slow. Column 4 contains the results obtained by sieving according to standard specifications, using, however, a single brass washer about ¾ inch in diameter to aid in breaking up the small lumps of fine material. Column 5 shows the effect of using six $\frac{3}{16}$-inch steel balls in place of the washer.

While the determinations are too few in number to show decided differences, the order in which the results actually occur is interesting. From the lowest to the highest amounts passing the sieve, the order is as follows:

1. Sieving with a washer on the sieve.
2. Sieving with steel balls on the sieve.
3. Sieving at 250 strokes per minute.
4. Sieving at 200 strokes per minute.
5. Sieving at 150 strokes per minute.

Thus the trials indicate that the simplest and easiest method—that is, sieving at the moderate rate of about 150 strokes per minute—gives the maximum percentage of cement passing the sieve. The somewhat erratic results obtained by the use of the washer and the balls, which might have been anticipated to give the highest values, are seen to be the lowest; and the variations are to be accounted for by the uncertainty of the stopping point. The use of washer and balls seems to increase the irregularity of the amounts obtained in successive minutes toward the end of the sieving, so that one may naturally stop somewhat earlier than he would if the amounts were decreasing regularly. It is evident, of course, that for every minute over or under sieving, the error introduced is approximately 0.1 per cent. On this basis the maximum limit of tolerance for the best work can hardly be less than 0.2 per cent, since the most careful observer may readily be one minute short or one minute over.

The fact that appreciably more cement passes the sieve at 150 strokes per minute than at 250 strokes per minute is no doubt due to the more rapid horizontal motion of the sieve in the latter case, whereby particles just under the smallest size retained have less opportunity to fall through the sieve openings than when the sieve is moving at the slower rate.

In all sieving tests it is tacitly assumed that the specifications need not be closely followed until the greater part of the fine material has already been sieved through, that is, the final result is assumed to be independent of the manner in which the first partof the sieving has been performed. This is no doubt justified in hand sieving when no washers or balls are used to hasten the process, but one may well question the assumption when vigorous methods are used, as in most routine work. In all trials reported in Table 2, the specifications were followed throughout the entire time of sieving.

It may of course be possible to form an estimate of the relative sieving value of a sieve from the direct measurements made upon it of the number and diameters of the warp and shoot wires, and the uniformity of spacing of the wires. The establishment, however, of a hard and fast demerit system for calculating the sieving value involves much guesswork, and the attempts thus far made at the Bureau of Standards to devise such a system have been only partially successful. It is not therefore worth while to go into the details of the manner in which the demerits have been assigned other than to state that consideration was given to all factors which affect the variations in size and distribution of the openings.

TABLE 3

Relation Between Value of Sieves as Actually Tested and Estimated Value Based on Sieve Measurements

Sieve	Sieve value	Demerits	Sieve	Sieve value	Demerits
1	80.16	− 408	7	80.55	− 548
2	80.30	+1312	8	80.63	−1386
3	80.32	+1304	9	80.75	− 188
4	80.46	−2363	10	80.93	−1573
5	80.49	−1101	11	80.94	−2340
6	80.52	−1150	12	81.03	−3135

Table 3 gives the average sieving values of the sieves listed in Table 1, together with their demerits arbitrarily assigned from analysis of direct cloth measurements on the sieves. For convenience in comparing the observed and calculated values, the table is arranged in order of the sieving values, and the results are

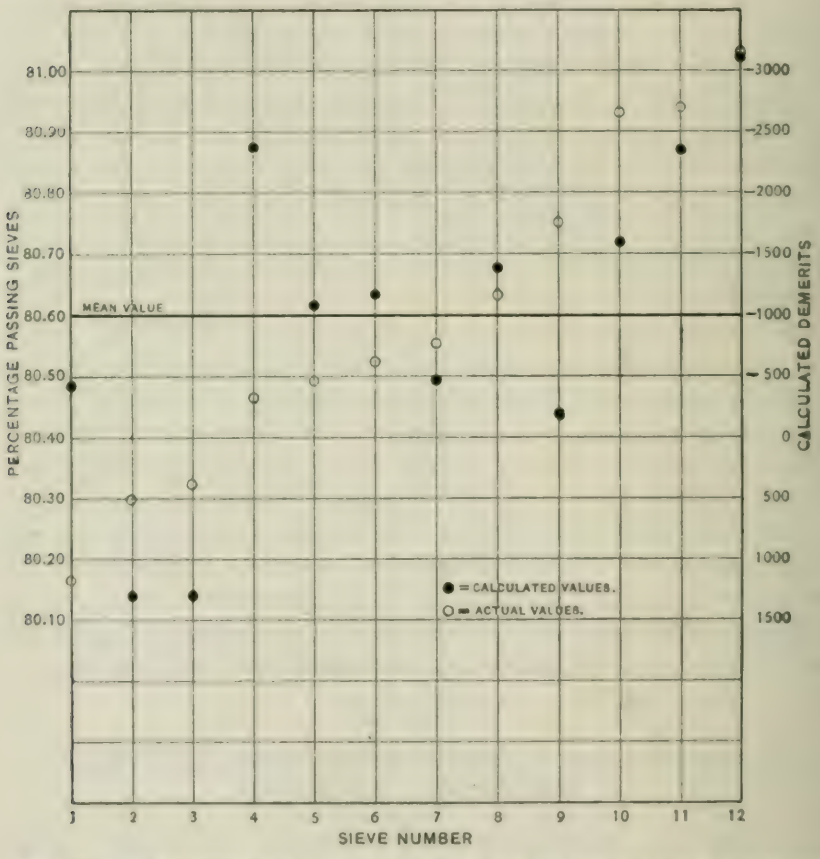

Fig. 1.—*Relation between value of sieves as actually tested and estimated value based on sieve measurements*

plotted in Fig. 1. The observed values are put in directly on the vertical lines passing through the numbers of the sieves, which are laid off at equal intervals on the horizontal axis. The calculated values are obtained in the following way:

It is seen that the total range of demerits is from —1312 to +3135, or 4447. Corresponding to this is a total range of 0.87 per cent in the observed sieving values, so that 0.01 per cent in the observed sieving value is approximately equal to 50 demerits. In the figure the total range of demerits is laid off to equal the total range of sieving values, so that all intermediate values may be definitely read off either as demerits or as calculated sieving values.

While the agreement is not startling, it may be remarked that in only three cases out of twelve is the calculated value more than 0.2 per cent from the observed value, and the maximum difference between calculated and observed values is only about 0.4 per cent (sieve No. 4). Moreover, in this series of tests the weight of the observed values is not so great that we may consider them to be much more reliable than those from the cloth measurements.

The foregoing discussion has been based entirely on the results obtained with the 12 No. 200 standard sieves listed in Table 1, and does not apply to the determinations on the No. 100 sieves.

TABLE 4

Results of Sieving Tests Made by Four Observers on 12 Standard No. 100 Sieves

Sieve	Observers					Average	Maximum variation from average
	A	B	C	D	E		
1	96.28	96.48	96.44	96.64	.....	96.46	0.18
2	96.24	96.50	96.58	96.70	.....	96.50	.26
3	96.22	96.48	96.44	.....	96.86	96.50	.36
4	96.46	96.50	96.42	96.70	.....	96.52	.18
5	96.32	96.58	96.48	96.72	.....	96.52	.20
6	96.30	96.74	96.50	96.68	.....	96.56	.26
7	96.52	96.68	96.52	96.44	96.74	96.58	.14
8	96.48	96.56	96.58	96.74	.....	96.59	.15
9	96.54	96.60	96.56	96.66	.....	96.59	.07
10	96.54	96.48	96.42	96.90	.....	96.59	.31
11	96.64	96.64	96.72	96.64	.....	96.66	.06
12	96.59	96.68	96.68	96.96	.....	96.73	.23
Average	96.43	96.58	96.53	96.71	.....	96.56	.20
Personal equation	+.13	—.02	+.03	—.15	.....	.....	.....

Table 4 is similar to Table 1, containing the results obtained by four observers using 12 "standard" No. 100 sieves. The same method of examination enables us to state that a single determination of fineness on the No. 100 sieve is likely to be at least 0.2 of 1 per cent in error. This value is of course less than the corresponding value for the No. 200 sieve, owing to the smaller quantity of material of this grade, which therefore gives a more definite stopping point in the sieving. Similarly, the range of differences that may be expected between standard sieves is less than that for the No. 200 sieves, being in this case from 96.46 per cent to 96.73 per cent, or 0.27 per cent. The maximum correction of a "standard" No. 100 sieve to the ideal No. 100 sieve therefore appears to be of the order of 0.2 per cent.

A striking agreement is also noted between the "personal equations" as given in Tables 1 and 4, the operators being the same in each case.

TABLE 5

Results of Sieving Tests Made on Nine Standard No. 200 Sieves

Sieve	Observers			Average	Maximum variation from average
	A	B	C		
1	80.26	79.76		80.01	0.25
2	80.66	80.48		80.57	.09
3		81.18	80.68	80.93	.25
4	80.83	81.06		80.94	.12
5		81.30	80.78	81.04	.26
6	81.36	81.36		81.36	.00
7	81.50	81.28		81.39	.11
8	81.56	81.80		81.68	.12
9	81.70	81.82		81.76	.06
Average	81.12	81.12	80.73	81.08	.14

TABLE 6

Results of Sieving Tests Made on Thirteen Rejected No. 200 Sieves

Sieve	Observers			Average	Maximum variation from average
	A	B	C		
1	80.96	80.10	.....	80.53	0.43
2	80.78	79.96	81.14	80.63	.67
3	80.80	80.68	.....	80.74	.06
4	80.92	80.96	.....	80.94	.02
5	81.12	81.06	.....	81.09	.03
6	81.36	80.88	.....	81.12	.24
7	81.48	81.12	.....	81.30	.18
8	81.64	81.12	.....	81.38	.26
9	81.18	81.68	.....	81.43	.25
10	81.46	81.60	.....	81.53	.07
11	82.16	81.42	.....	81.79	.37
12	81.84	81.80	.....	81.82	.02
13	81.98	82.20	.....	82.09	.11
Average	81.36	81.12	81.14	81.26	.21

Tables 5 and 6 contain the results obtained mainly by two observers on 22 No. 200 sieves, 13 of which failed to meet the requirements of standard sieves. These rejected sieves were not of as poor quality as some which have been tested in the laboratory, especially those tested prior to the issuance of the Bureau's sieve specifications.

While in general it may be expected that the rejected sieves will show larger differences from the ideal sieve than the "standard" sieves, this is not necessarily the case. Thus a single bad quarter or half inch strip in the wire cloth may cause the rejection of a sieve, whereas the bad strip may have no appreciable effect on the sieving value. In other words a rejected sieve may frequently have a better sieving value than a standard sieve, and examples of such cases are shown in Tables 5 and 6.

Examination of the tables shows that the observers A and B obtained fairly consistent results in sieving. It is interesting to note that the observed range in sieving values of the standard sieves given in Table 5 is from 80.01 per cent to 81.76 per cent, or 1.75 per cent; that is, nearly twice as great a value as observed in the first lot of sieves.

TABLE 7

Results of Sieving Tests Made on Nine Standard No. 100 Sieves

Sieve	Observers			Average	Maximum variation from average
	A	B	C		
1	95.70	95.76	.....	95.73	0.03
2	95.88	96.06	.....	95.97	.09
3	95.82	96.28	.....	96.05	.23
4	96.00	96.22	.....	96.11	.11
5	96.00	96.26	.....	96.13	.13
6	95.92 95.90	96.42 96.30	.....	96.14	.28
7	96.06	96.30	.....	96.18	.12
8	96.06	96.36	.....	96.21	.15
9	96.12	96.44	.....	96.28	.16
Average	95.95	96.24	.....	96.09	.14

TABLE 8

Results of Sieving Tests Made on Thirteen Rejected No. 100 Sieves

Sieve	Observers			Average	Maximum variation from average
	A	B	C		
1	95.60	95.80	96.00	95.80	0.20
2	95.87	95.98	.....	95.92	.06
3	95.92	96.04	.....	95.98	.06
4	95.95	96.04	.....	96.00	.05
5	95.90	96.10	.....	96.00	.10
6	96.06	96.12	.....	96.09	.03
7	95.95	96.30	.....	96.12	.18
8	95.96	96.38	.....	96.17	.21
9	96.18	96.18	.....	96.18	.00
10	96.02	96.40	.....	96.21	.19
11	96.20	96.26	.....	96.23	.03
12	96.26 96.42	96.50	.....	96.39	.13
13	96.26	96.68	96.26 96.38	96.40	.28
Average	96.04	96.21	96.21	96.11	.12

Tables 7 and 8 give the results obtained mainly by two observers on 22 No. 100 sieves, 13 of which were rejected as "standard" sieves.

Of those which passed the requirements, the lowest sieving value observed is 95.73 per cent and the highest 96.21 per cent, a range of 0.48 per cent. This, again, is nearly twice the corresponding value for the first lot of sieves, but the most striking result is that the highest sieving value in this lot is 0.25 per cent below the lowest sieving value in the first lot.

The personal equations for observers A and B are seen to agree fairly well in Table 4 as compared with Tables 7 and 8, but those given in Table 1 do not agree with those in Tables 5 and 6.

IV. CONCLUSIONS

In reviewing the results of the foregoing tests the following conservative estimates may be given:

1. Employing the present standard method of sieving, the greatest attainable accuracy in single fineness determinations of normal Portland cement on a standard No. 200 sieve, that is, the greatest attainable accuracy in checking uniformity of samples is about 0.2 per cent.

2. "Standard" No. 200 sieves may differ in their sieving values by considerable amounts, such that their corrections to the ideal No. 200 sieve may be at least as great as 0.7 per cent.

3. Errors of at least 0.5 per cent may be looked for in single fineness determinations of normal cements on a standard No. 200 sieve when made in the usual routine manner.

4. Deviations exist in the sieving values of "standard" No. 100 sieves, of a magnitude, roughly, one-half the corresponding values for No. 200 sieves as given above.

5. "Personal equation" appears to be appreciable in hand sieving, as in most laboratory operations, the observed values being as great as 0.3 per cent.

6. The rating of a sieve by some system of demerits assigned from direct measurements appears to be an interesting possibility, and worthy of further study. Should a system be worked

out to give reliable indications say within 0.2 per cent or 0.3 per cent of the observed sieving value of a sieve, it will add greatly to the value of the certificate now furnished with standard sieves.

It seems evident from the foregoing that both sieving tests and the interpretation of measurements on sieves are subject to considerable discrepancies, and the question arises as to whether some other more reliable method of determining fineness can not be made available. The sieve at best is a measure of the *coarseness* of finely ground material rather than the *fineness*, and experiments now in progress at the Bureau of Standards indicate that air separation will offer a more satisfactory means of determining fineness than mechanical sieving.

In conclusion it may be stated that a tolerance of 1 per cent from the specification should be allowed with the No. 200 sieve and 0.5 per cent from the specification with the No. 100 sieve, every care being taken to conduct the test in strict accordance with standard methods. These tolerances should be considered as minimum values since they are based upon the results obtained by careful and experienced observers; therefore it should be emphasized that greater differences are possible in ordinary routine testing.

WASHINGTON, August 1, 1913.

DEPARTMENT OF COMMERCE

TECHNOLOGIC PAPERS

OF THE

BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

No. 30

VISCOSITY OF PORCELAIN BODIES

BY

A. V. BLEININGER, Ceramic Chemist

and

PAUL TEETOR, Laboratory Assistant

Bureau of Standards

[NOVEMBER 20, 1913]

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1914

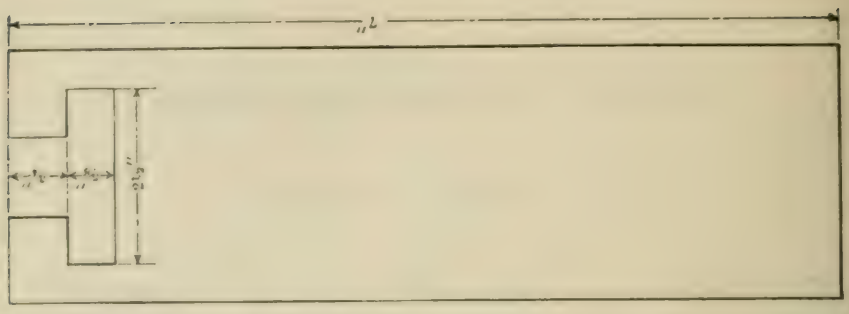
VISCOSITY OF PORCELAIN BODIES

By A. V. Bleininger and Paul Teetor

The vitrification of ceramic bodies requires for its explanation two assumptions, the existence of a considerable superficial force tending to contract the mass, and lowered viscosity or softening which will permit the displacement and rearrangement of the molecules. The existence of surface tension must be considered as proven in the light of many well-known physical phenomena. Likewise, there can be no doubt as to the softening of the body, since the deformation observed only too frequently clearly indicates such a condition.

Owing to the fact that no numerical values are available with reference to the degree of softening of ceramic bodies, it was thought desirable to carry on experiments with the purpose of determining the degree of viscosity reached by a series of bodies of the porcelain type. As a measure of the viscosity, the deformation under tensile stress was used. For this purpose specimens of porcelain body were made up of such shape that they could be hung from a fire-clay grid and a weight attached to the bottom. The shape and dimensions of the pieces are shown in the diagrams of Fig. 1. The length of the square bar between the end pieces was 4.5 inches and the width 1.112 inches, mold measurements. It was desired to have specimens possessing a cross section of approximately 1 square inch after burning them to vitrification.

The load was applied to each bar (after firing to cone 10) by means of a fire-clay piece provided with a groove into which fitted the bottom part of the porcelain. It was decided to maintain the tensile load as closely at 5 pounds per square inch as possible. After burning the test bars their cross section was measured accurately by means of a micrometer caliper and the average cross section computed, based upon 10 measurements. For each bar



FIRE CLAY WEIGHT

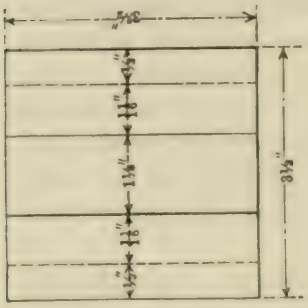
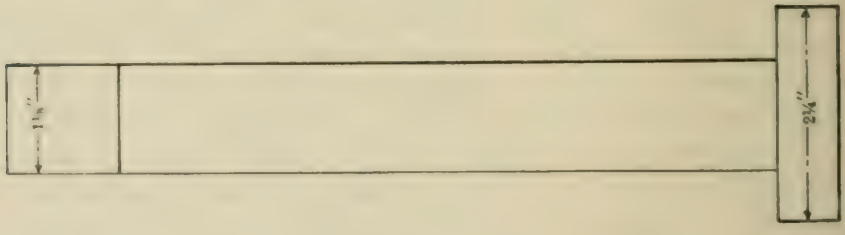
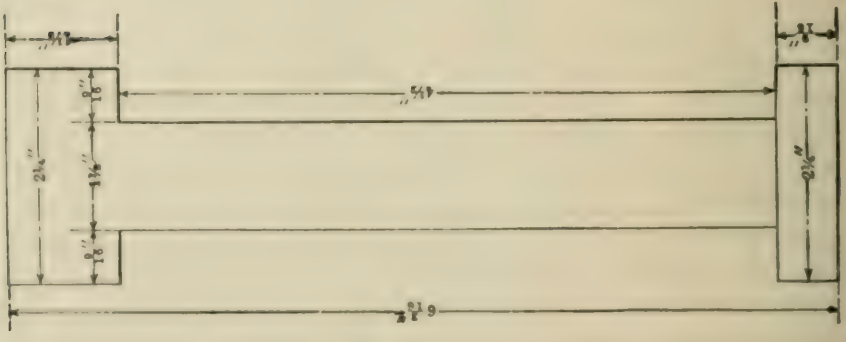


Fig. 1





Porcelain Test Piece

the weight of the corresponding fire-clay load piece was then adjusted by chipping so that the initial tensile strain was 5 pounds per square inch. The elongation was determined by measuring the distance between two fine lines 9 cm. apart.

The porcelain series embraced composition ranging from 35 to 50 per cent of clay and from 10 to 25 per cent of feldspar. The clay material was introduced as North Carolina kaolin, Georgia kaolin, and Tennessee No. 3 ball clay in the proportions of 5: 1 : 1. In Table 1 the chemical analyses of the raw materials are given and in Table 2 the composition of the bodies.

The body constituents were ground together in the slip state in the ball mill for two hours, then screened and filter pressed. After wedging the mass it was pressed into the shape shown. After thorough drying all of the specimens were fired to cone 10 before being subjected to the tension tests. The bars were then suspended from H-shaped fire-clay grids, placed firmly upon fire-brick piers and the proper weight piece attached to each. The firing for the tensile tests was carried to the following temperatures: 1065°, 1100°, 1125°, 1160°, 1190°, 1220°, 1250°, 1280°, and 1310° C. Up to 800° the burning was carried at a convenient rate, but from this point on great care was taken to raise the temperature at the rate of $33\frac{1}{3}°$ per hour. Firing was stopped as soon as the proper temperature was reached. No elongation was observed until the 1160° burn.

The numerical results of the work are compiled in Table 3. The ink test was applied to the bodies after burning them to the maximum temperature, by noting the absorption of ink after washing off the spot with oxalic acid and water.

It will be noted from the table that complete vitrification, as measured by the ink absorption, takes place in no case with less than 19 per cent of feldspar.

It is interesting to observe, also, that softening occurs at as low a temperature as 1160° only in the case of the larger feldspar contents, 22 and 25 per cent, and even these amounts do not lower the viscosity with the maximum clay content.

Small percentages of feldspar, 10 and 13 per cent, bring about softening only with low clay content, 35 per cent, and then only at 1280°. Even with 16 per cent feldspar, elongation does not

appear until 1250° to 1280° has been reached. High feldspar contents, on the other hand, show deformation at as low a temperature as 1160° with 35 per cent of clay. The decreasing effectiveness of the fluxing constituent in bringing about softening with increasing clay is clearly shown, inasmuch as with 50 per cent of clay and 25 per cent feldspar elongation does not begin before 1220°.

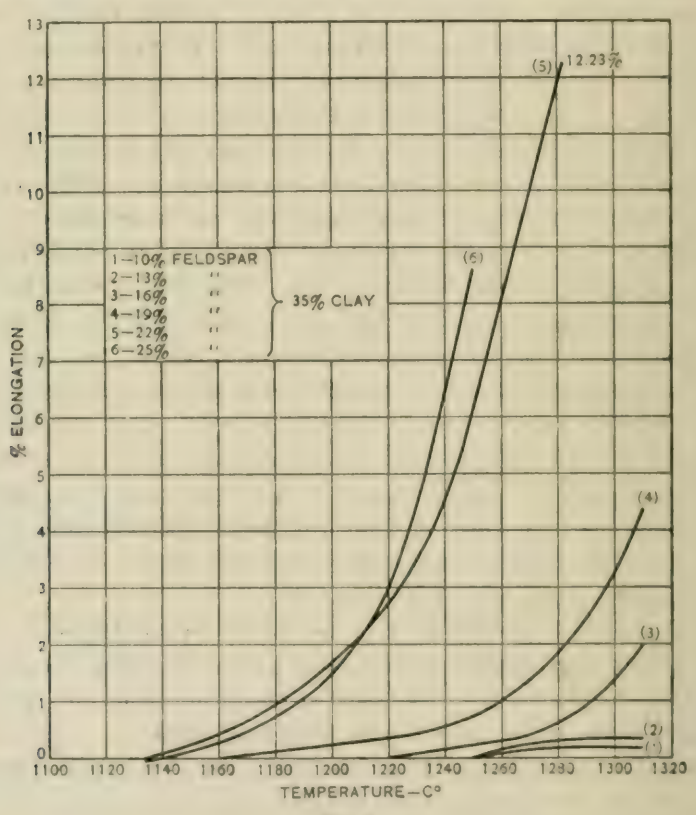


Fig. 2

The diagrams of Figs. 2, 3, 4, and 5 illustrate the elongation behavior of the bodies for the clay contents of 35, 40, 45, and 50 per cent.

In the 35 per cent clay series, Fig. 2, a sudden decrease in viscosity seems to occur between 19 and 22 per cent of feldspar. The latter amount is clearly excessive for this body. It would seem as if up to 19 per cent the feldspar formed a viscous solution

with the other constituents, while at 22 per cent it was in excess and, due to its own low viscosity, caused the body to soften rapidly.

From this it appears that it is rather important to fix the feldspar content at the lowest value consistent with the desired physical properties.

In the 40 per cent clay series, Fig. 3, the curves are grouped together much more closely and no such sharp break in viscosity is observed, for which behavior the increased clay content is undoubtedly responsible. The elongation values also are smaller—

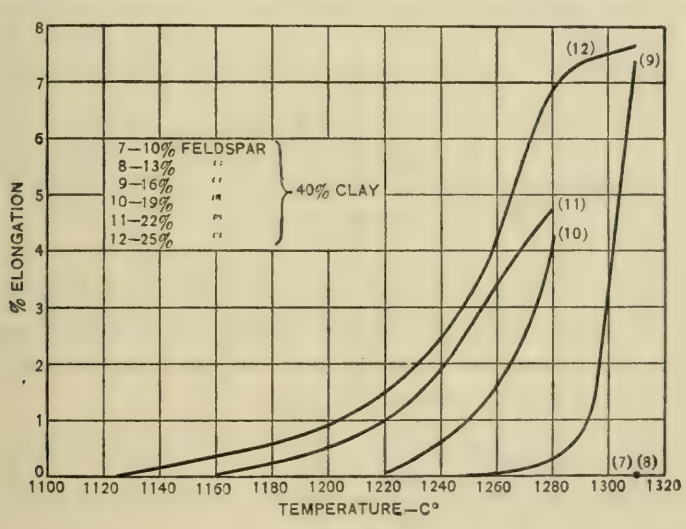


Fig. 3

i. e., the viscosities greater. The curves, however, are quite steep, indicating a rapid decrease in viscosity or softening with temperature which is not a desirable condition.

In Fig. 4 not only is a regular gradation observed between the different feldspar contents of the 45 per cent clay series, but the curves are very much less abrupt and thus indicate more gradual changes in viscosity between given temperatures. The rate of viscosity change is proportional to the feldspar content. The deformation values are considerably lower than for the 40 per cent clay series.

The diagram of Fig. 5 (50 per cent clay series) shows a marked drop in the deformation values from the preceding bodies. The viscosity thus has increased very decidedly, which means lessened

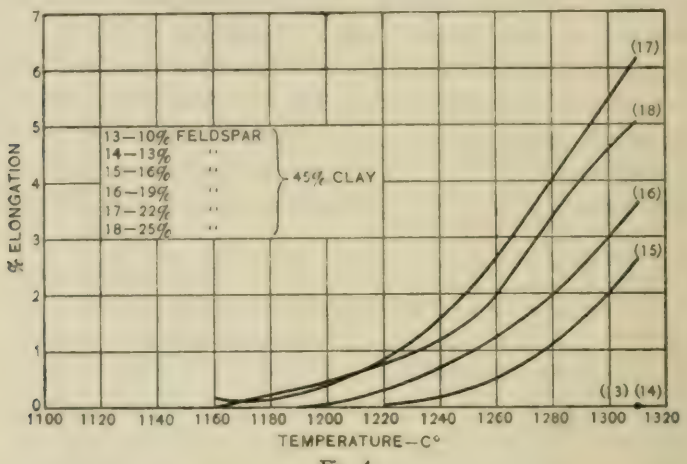


Fig. 4

deformation. It is noted also that the effect of the feldspar increases is very much less marked than in the preceding cases. The rate of decrease in viscosity with rise in temperature also is very much less pronounced in this case.

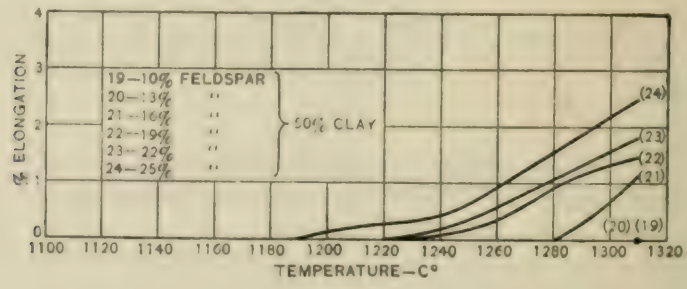


Fig 5.

From the foregoing results it seems, then, that for the temperatures and the raw materials under consideration, complete vitrification is not possible with less than 19 per cent of feldspar. Excess of feldspar is undesirable owing to the lowered viscosity brought about by it.

The higher the clay content the less marked does the effect of feldspar become. A sharp line of demarcation appears between the bodies containing less than 45 per cent clay and those of higher clay content. The former possess a very much higher temperature coefficient of viscosity decrease and hence are more subject to deformation. A lower clay content than 45 per cent is therefore undesirable and may explain the difficulties experienced with bodies of the Seger porcelain type. The strength of porcelain bodies under tensile stress, at the kiln temperatures considered, has been found to be quite low, approaching 5 pounds per square inch quite closely with maximum elongation and is but a small fraction of the tensile strength at ordinary temperatures. As to the permissible numerical elongation value under a load of 5 pounds per square inch, no exact deductions can be made, but it probably lies between 5 and 6 per cent.

This method of studying bodies is capable of producing valuable results and might with advantage be applied to clays and other mixtures. In further work along this line a different style of bar is being used, resembling at the ends the shape of cement briquettes. The length of the straight portion is 4 inches.

TABLE 1

	North Carolina kaolin	Tennessee ball clay	Georgia kaolin	Feldspar	Flint
	Per cent	Per cent	Per cent	Per cent	Per cent
Silica	45.84	50.80	45.69	70.79	99.23
Alumina	38.46	32.09	37.52	16.75	.32
Ferric oxide	.57	1.56	.53	.22	.10
Titanium oxide	.11	1.23	1.61	.....	.....
Calcium oxide	.19	.18	.18	.24	.08
Magnesium oxide	.08	.40	.25	.18	.13
Sodium oxide	.07	.38	.11	3.29	.....
Potassium oxide	.35	1.14	.20	8.26	.....
Loss on ignition	14.44	12.49	14.05	.46	.22
Total	100.11	100.27	100.14	100.19	100.08

TABLE 2

Composition of Bodies

Number	Per cent clay	Per cent feldspar	Per cent flint
1	35	10	55
2	35	13	52
3	35	16	49
4	35	19	46
5	35	22	43
6	35	25	40
7	40	10	50
8	40	13	47
9	40	16	44
10	40	19	41
11	40	22	38
12	40	25	35
13	45	10	45
14	45	13	42
15	45	16	39
16	45	19	36
17	45	22	33
18	45	25	30
19	50	10	40
20	50	13	37
21	50	16	34
22	50	19	31
23	50	22	28
24	50	25	25
25 [1]	.....	.....	.....

[1] Commercial porcelain body.

TABLE 3

Number	Per cent elongation at degrees centigrade						Ink test after firing to 1310°	Remarks
	1160°	1190°	1220°	1250°	1280°	1310°		
1					0.13	0.13	Strong stain	
2					.25	.27	do	
3				0.20	.56	2.02	Stained	
4		0.14	0.34	.76	1.83	4.35	No stain	
5	0.39	1.29	2.79	6.17	12.23		do	Partly pulled in two at 1280°
6	.22	1.04	3.02	8.56			do	Partly pulled in two at 1250°
7							Strong stain	
8							Stain	
9					.28	7.40	Strong stain	Partly pulled apart at 1310°
10				.94	4.22		Faint stain	Partly pulled apart at 1280°
11		.36	.93	2.72	4.77		No stain	
12	.34	.62	1.40	3.14	7.01	7.62	do	Pulled apart, 1310°
13							Strong stain	
14							Stained	
15				.28	1.04	2.66	do	
16			.28	.95	1.99	3.65	No stain	Broke, 1310°
17	.17	.25	.85	2.03	4.09	6.14	do	
18		.34	.73	1.52	3.37	5.02	do	
19							Strong stain	
20							Stain	
21						1.15	Faint stain	
22				.17	.96	1.49	No stain	
23				.25	1.01	1.20	do	
24			.26	.59	1.53	2.49	do	
25			.14	.39	2.01	4.08	do	Do.

WASHINGTON, November 20, 1913.

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S. W. STRATTON, DIRECTOR

No. 31

SOME LEADLESS BOROSILICATE GLAZES MATURING AT ABOUT 1100° C

BY

E. T. MONTGOMERY, Assistant Ceramic Chemist

Bureau of Standards

[DECEMBER 15, 1913]

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SOME LEADLESS BOROSILICATE GLAZES MATURING AT ABOUT 1100° C

BY

E. T. MONTGOMERY, Assistant Ceramic Chemist

Bureau of Standards

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I. OBJECT OF THE INVESTIGATION

The glazes used on white-ware are composed of borosilicates of the alkalies, lime, lead, and alumina, which are applied to a body previously fired to the desired maturing point approaching vitrification more or less closely. The same type of glaze is also employed with American porcelain and the English bone china as distinguished from the Austrian, French, and German products where, because of the low biscuit and high glost firing temperatures, it is possible to use leadless glazes. The use of the latter type is feasible only when temperatures above cone 8 (approximately 1170° C) are involved. In the production of American and English tableware it is essential, therefore, that the maturing point of the glazes be considerably below the vitrification temperature of the body (about cone 3, approximately 1100° C) in

order to avoid undue softening of the body and consequent deformation and loss. To accomplish this purpose such low-fusing glasses as borosilicates containing lead oxide are necessarily employed. At the same time the long temperature range, brilliancy, and low viscosity of the lead glazes are desirable qualifications.

The use of lead oxide, commonly introduced as the carbonate, has given rise to a wide-spread agitation concerning the poisonous nature of the compound and its deleterious influence upon the health of the workmen under conditions permitting careless operation and neglect of ordinary sanitary precautions. A study of American white-ware potteries shows, however, that such conditions as have been described as existing in European works do not prevail and that in reality the ill effects due to plumbism are very slight in extent. It can not be denied that there is a potential danger, but the enforcement of rules concerning ordinary cleanliness and ventilation suffices to prevent lead poisoning.

Two alternatives which have been suggested in regard to the employment of lead glazes are, the preliminary fusion of the lead oxide with silica, borax, boric acid, feldspar and whiting to form a practically insoluble plumbiferous borosilicate glass (frit) which when ground together with kaolin and additional flint forms the desired glaze, and secondly the complete elimination of the objectionable lead.

The first offers a fairly satisfactory solution of the problem, but introduces difficulties in the application of the glaze on the ware. With our present knowledge of flocculating and deflocculating reagents this plan should offer no insurmountable obstacle. The second alternative is not sufficiently justified at the present time.

Chiefly on account of the poisonous nature of the lead compounds used in making the usual type of white-ware glaze, the subject of leadless glazes has aroused the interest and has received the serious attention of both technical ceramists and manufacturers for many years. As has been set forth, white-ware and china glazes, made with lead compounds, either fritted in or added raw, may be used under proper conditions and by observing

suitable precautions, without any danger to the health of the operatives.

On the other hand, wherever leadless glazes can be developed and used, such precautions, which in themselves increase the cost of manufacture, do not have to be taken and every element of risk is thus eliminated to the mutual advantage of both employer and employee. Also while lacking some of the valuable characteristics and qualities of lead glazes, it can be shown that leadless glazes have a few distinct advantages of their own.

The question, therefore, of lead glazes vs. leadless glazes for china or white-ware becomes one of purely technical and practical interest involving the factors of working properties, quality of finished product, and cost. It becomes then the purpose of the present work to investigate the merits of the various types of leadless glaze thus far reported, to study their properties and possibilities, to improve them if possible, and to make a general comparison from a technical standpoint, between lead and leadless glazes for white-ware and china at a glost heat of Seger cone 3 (about 1100° C to 1120° C in a 24-hour burn).

II. DESCRIPTION OF THE WORK

1. REQUIREMENTS TO BE MET

A leadless glaze that can be considered at all practical must meet the following requirements:

(*a*) When suitably prepared and handled it must work equally as well as a lead glaze in the dipping room.

(*b*) It must have a sufficiently long heat range for all practical purposes in firing and flow over minor defects well enough so that the per cent of "seconds" does not run appreciably higher than in the case of lead glazes.

(*c*) It must permit the use of as wide a range of both underglazes and on-glaze colors as do lead glazes.

(*d*) It must produce a finished piece of ware of at least equally pleasing appearance and equally as durable as that produced by the use of lead.

(*e*) The cost of the glazing operation as a whole, including all losses chargeable to the glaze, must not exceed that for lead glazes.

2. OUTLINE OF THE INVESTIGATION

There have been practically no further contributions of importance to our knowledge of leadless glazes from a technical standpoint since Seger [1] published his valuable researches on the subject.

Seger's work and the general rules for leadless glazes which he deduced were, therefore, closely followed in outlining the work. This information, together with a general knowledge of what this type of glaze should be, made only a short series of glazes necessary, as it was not the writer's purpose to try to lay down the limits of composition of these glazes, but to develop the best leadless glazes possible. The first series outlined was for the purpose of determining the best type formula and the suitability of the RO fluxes selected. The second series was designed to further improve the best glaze developed in the first series. All glazes were tested over six standard underglaze colors of known composition, and all properties were studied in comparison with a standard lead white-ware or china glaze used over a half of each trial piece, the other half being dipped in the leadless test glaze.

Series No. I [2]

.35 Al_2O_3 GROUP

Glaze B1				Frit			
.25 K_2O				.1875 K_2O			
.05 Na_2O				.0625 Na_2O			
.50 CaO				.5000 CaO			
.10 BaO	.35 Al_2O_3	3.1 SiO_2		.1250 BaO	.1875 Al_2O_3	2.535 SiO_2	
.05 MgO		0.125 B_2O_3		.0625 MgO		.1565 B_2O_3	
.05 SrO				.0625 SrO			

.8 equiv. of frit used. Comb. wt. 259.7

[1] Leadless Glazes, H. A. Seger, Collected Works, vol. i, p. 453.

[2] The chemical formulæ are of an empirical nature and are used for the systematic presentation of the glaze compositions. It would be difficult to compare glazes or glasses if only their percentage composition were known. The computation of the formula has for its object the arrangement of the oxides into three groups. These are: Bases of the R_2O and RO type which always add up to unity; the sesqui oxides, R_2O_3 and the acids RO_2. This artifice makes possible the comparison of glazes with reference to acidity, fusibility, translucency, brilliancy, resistance to reagents, crazing, etc.

The formula is calculated from the composition, expressed in parts by weight, by dividing the molecular weight of each substance into its quantity and adding the quotients representing the R_2O and RO oxides. Each quotient is then divided by this sum. By arranging the values obtained in the three groups, the desired empirical formula results.

As an aid in the classification of glazes the acidity or oxygen ratio (O. R.) is frequently used. By this is meant the ratio of the atomic oxygen equivalent in the silica to that of the bases. Thus the oxygen ratio of the formula $RO.2Al_2O_3.3SiO_2$ is $6 \div 1.6 = 3.75$.

.35 Al_2O_3 GROUP—Continued

Glaze B2

			Frit		
.25 K_2O		3.1 SiO_2	.1875 K_2O		2.875 SiO_2
.05 Na_2O			.0625 Na_2O		
.50 CaO	.35 Al_2O_3		.5000 CaO	.1875 Al_2O_3	
.10 BaO		0.35 B_2O_3	.1250 BaO		.4375 B_2O_3
.05 MgO			.0625 MgO		
.05 SrO			.0625 SrO		

.8 equiv. of frit used. Comb. wt. 299.8

Glaze B3

			Frit		
.25 K_2O		3.1 SiO_2	.1875 K_2O		2.875 SiO_2
.05 Na_2O			.0625 Na_2O		
.50 CaO	.35 Al_2O_3		.5000 CaO	.1875 Al_2O_3	
.10 BaO		0.5 B_2O_3	.1250 BaO		.625 B_2O_3
.05 MgO			.0625 MgO		
.05 SrO			.0625 SrO		

.8 equiv. of frit used. Comb. wt. 312.9

.40 Al_2O_3 GROUP

Glaze C1

			Frit		
.30 K_2O		3.25 SiO_2	.2500 K_2O		3.0625 SiO_2
.50 CaO			.5000 CaO		
.10 BaO	.40 Al_2O_3		.1250 BaO	.25 Al_2O_3	
.05 MgO		0.35 B_2O_3	.0625 MgO		.4375 B_2O_3
.05 SrO			.0625 SrO		

.8 equiv. of frit used. Comb. wt. 319.4

Glaze C2

			Frit		
.30 K_2O		3.7 SiO_2	.2500 K_2O		3.625 SiO_2
.50 CaO			.5000 CaO		
.10 BaO	.40 Al_2O_3		.1250 BaO	.25 Al_2O_3	
.05 MgO		0.5 B_2O_3	.0625 MgO		.625 B_2O_3
.05 SrO			.0625 SrO		

.8 equiv. of frit used. Comb. wt. 366.3

.50 Al_2O_3 GROUP

Glaze D1

			Frit		
.40 K_2O		4.0 SiO_2	.3750 K_2O		4.0 SiO_2
.40 CaO			.3750 CaO		
.10 BaO	.50 Al_2O_3		.1250 BaO	.375 Al_2O_3	
.05 MgO		0.5 B_2O_3	.0625 MgO		.625 B_2O_3
.05 SrO			.0625 SrO		

.8 equiv. of frit used. Comb. wt. 406.3

Glaze D2

			Frit		
.40 K_2O		4.0 SiO_2	.3750 K_2O		4.0 SiO_2
.40 CaO			.3750 CaO		
.10 BaO	.50 Al_2O_3		.1250 BaO	.375 Al_2O_3	
.05 MgO		1.0 B_2O_3	.0625 MgO		1.25 B_2O_3
.05 SrO			.0625 SrO		

.8 equiv. of frit used. Comb. wt. 450.1

Glaze D3

			Frit		
.40 K_2O		3.5 SiO_2	.3750 K_2O		3.375 SiO_2
.40 CaO			.3750 CaO		
.10 BaO	.50 Al_2O_3		.1250 BaO	.375 Al_2O_3	
.05 MgO		1.0 B_2O_3	.0625 MgO		1.25 B_2O_3
.05 SrO			.0625 SrO		

.8 equiv. of frit used. Comb. wt. 412.6

.60 Al_2O_3 GROUP

Glaze E1		Frit
.40 K_2O		.3750 K_2O
.40 CaO		.3750 CaO
.10 BaO	.60 Al_2O_3 { 4.0 SiO_2 ; 0.5 B_2O_3	.1250 BaO
.05 MgO		.0625 MgO
.05 SrO		.0625 SrO

.50 Al_2O_3 { 4.0 SiO_2 ; .625 B_2O_3

.8 equiv. of frit used. Comb. wt. 419.1

Glaze E2		Frit
.40 K_2O		.3750 K_2O
.40 CaO		.3750 CaO
.10 BaO	.60 Al_2O_3 { 4.0 SiO_2 ; 1.0 B_2O_3	.1250 BaO
.05 MgO		.0625 MgO
.05 SrO		.0625 SrO

.50 Al_2O_3 { 4.0 SiO_2 ; 1.25 B_2O_3

.8 equiv. of frit used. Comb. wt. 462.8

Glaze E3		Frit
.40 K_2O		.3750 K_2O
.40 CaO		.3750 CaO
.10 BaO	.60 Al_2O_3 { 3.5 SiO_2 ; 1.0 B_2O_3	.1250 BaO
.05 MgO		.0625 MgO
.05 SrO		.0625 SrO

.50 Al_2O_3 { 3.375 SiO_2 ; 1.25 B_2O_3

.8 equiv. of frit used. Comb. wt. 425.30

A careful study of Seger's results [3] on leadless glazes, of Stull's work [4] on whiteware glazes low in lead, and of many successful whiteware and china glazes shows clearly that the best glazes of this type, lead or leadless, occur at or very near to an oxygen ratio of 1 : 2 when B_2O_3 is figured as a sesquioxide base. Before discussing the above glaze and frit formulae in detail the location of these glazes with reference to the 1 : 2 oxygen ratio line is shown in the following diagram, Fig. 1.

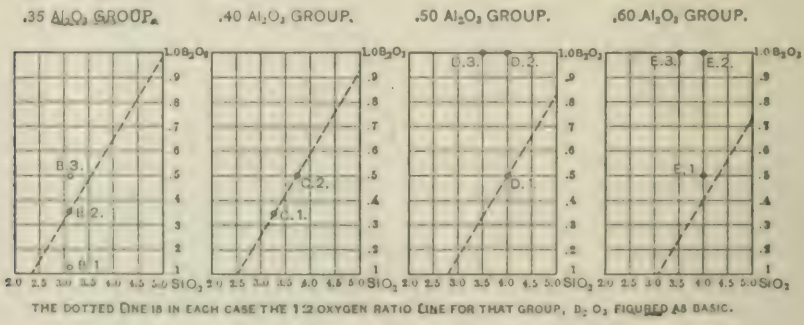

Fig. 1.—*Diagram showing location of glazes produced in field of compositions*

The glazes of series No. I are divided into four groups with increasing Al_2O_3 contents as follows: Group B, with .35 Al_2O_3; group C, with .40 Al_2O_3; group D, with .50 Al_2O_3; and group E, with .60

[3] Loc. cit. [4] Trans. Am. Cer. Society, vol. 12, p. 129.

Al_2O_3. In each group, with the RO and the SiO_2 constant except in one or two special cases, the B_2O_3 content is varied within the group. The frits, except in a few instances where it was impossible to do so, have the same oxygen ratio as the glazes. It must also be said in explanation that in this series the theoretical formula and combining weight of orthoclase feldspar was used instead of the actual one, as the analysis of the feldspar used was not available when the work was started, but was made later and used in calculating the glazes for series No. II.

In group B glaze B1 was suggested to the writer by Mr. Ernest Mayer, of the Mayer China Co. Glaze B2 is the same glaze with the B_2O_3 increased to .35 B_2O_3, which places this glaze on the 1 : 2 oxygen ratio line when B_2O_3 is figured as basic. Glaze B3 was taken from Mellor's report on leadless glazes and is one which he terms the old type of the leadless glaze. In this glaze the frit does not possess exactly the same oxygen ratio as the glaze, it being necessary to reduce the SiO_2 in the frit somewhat in order to leave sufficient SiO_2 to satisfy the raw constituents.

In group C both glazes C1 and C2 possess the oxygen ratio of 1 : 2, and both frits have the same ratio as the glazes.

In group D the formula for glaze D1, with the exception of the RO fluxes, was taken direct from Seger's work. Both the glaze and frit have a 1 : 2 oxygen ratio. Glaze D2 is one of Seger's with 1.0 B_2O_3. The frit has not the same oxygen ratio as the glaze, the SiO_2 being reduced a little for the same reason as in B3. Glaze D3 was designed from a glaze reported by Mellor [5] as the best type of leadless glaze thus far developed in England. The glaze reported is as follows:

$$\left.\begin{matrix} .55\ CaO \\ .45\ K_2O(Na_2O) \end{matrix}\right\}.55\ Al_2O_3 \left\{\begin{matrix} 3.5\ SiO_2 \\ 1.2\ B_2O_3 \end{matrix}\right.$$

Glaze D3 varies somewhat from this formula in order to make it conform to the rest of the group. It shows the effect of reducing the SiO_2 slightly from that used in glaze D2. The same remark on the SiO_2 in the frit applies here as in D2.

In group E we have group D duplicated except for the increase of Al_2O_3 from .50 Al_2O_3 to .60 Al_2O_3 in order to show the effect of further increasing this constituent in glazes high in B_2O_3.

[5] Trans. Eng. Cer. Society, 12, p. 7.

Series No. II

As glaze D1 proved to be the best glaze of series No. I, the second series was designed to further improve this glaze if possible by making changes in its RO fluxes. In this series the true formula and combining weight of the feldspar was used as determined by analysis. The other raw materials were so near to the theoretical in composition that no allowance was made for any of the materials excepting the feldspar.

Glaze D1a

$$\left.\begin{matrix}.40\ K_2O\\ .30\ CaO\\ .10\ BaO\\ .10\ MgO\\ .10\ SrO\end{matrix}\right\}.50\ Al_2O_3\left\{\begin{matrix}4.0\ SiO_2\\ .5\ B_2O_3\end{matrix}\right.$$

Frit

$$\left.\begin{matrix}.3750\ K_2O\\ .2500\ CaO\\ .1250\ BaO\\ .1250\ MgO\\ .1250\ SrO\end{matrix}\right\}.375\ Al_2O_3\left\{\begin{matrix}3.775\ SiO_2\\ .625\ B_2O_3\end{matrix}\right.$$

.8 equiv. of frit used. Comb. wt. 394.75

Glaze D1b

$$\left.\begin{matrix}.40\ K_2O\\ .30\ CaO\\ .10\ BaO\\ .10\ ZnO\\ .10\ SrO\end{matrix}\right\}.50\ Al_2O_3\left\{\begin{matrix}4.0\ SiO_2\\ .5\ B_2O_3\end{matrix}\right.$$

Frit

$$\left.\begin{matrix}.3750\ K_2O\\ .2500\ CaO\\ .1250\ BaO\\ .1250\ ZnO\\ .1250\ SrO\end{matrix}\right\}.375\ Al_2O_3\left\{\begin{matrix}3.775\ SiO_2\\ .625\ B_2O_3\end{matrix}\right.$$

.8 equiv. of frit used. Comb. wt. 399.9

Glaze D1c

$$\left.\begin{matrix}.40\ K_2O\\ .30\ CaO\\ .10\ BaO\\ .10\ MgO\\ .10\ ZnO\end{matrix}\right\}.50\ Al_2O_3\left\{\begin{matrix}4.0\ SiO_2\\ .5\ B_2O_3\end{matrix}\right.$$

Frit

$$\left.\begin{matrix}.3750\ K_2O\\ .2500\ CaO\\ .1250\ BaO\\ .1250\ MgO\\ .1250\ ZnO\end{matrix}\right\}.375\ Al_2O_3\left\{\begin{matrix}3.775\ SiO_2\\ .625\ B_2O_3\end{matrix}\right.$$

.8 equiv. of frit used. Comb. wt. 392.8

Glaze D1d

$$\left.\begin{matrix}.30\ K_2O\\ .10\ Na_2O\\ .30\ CaO\\ .20\ BaO\\ .10\ MgO\end{matrix}\right\}.50\ Al_2O_3\left\{\begin{matrix}4.0\ SiO_2\\ .5\ B_2O_3\end{matrix}\right.$$

Frit

$$\left.\begin{matrix}.2500\ K_2O\\ .1250\ Na_2O\\ .2500\ CaO\\ .2500\ BaO\\ .1250\ MgO\end{matrix}\right\}.375\ Al_2O_3\left\{\begin{matrix}3.775\ SiO_2\\ .625\ B_2O_3\end{matrix}\right.$$

.8 equiv. of frit used. Comb. wt. 397.0

In these glazes the molecular coefficients of the SiO_2 in the frits are a little less than in the frit of D1 for the reason that in using the true formula of the feldspar in series No. II, more SiO_2 is required to satisfy the feldspar in the raw portion of the glaze batch and, as no flint is added raw, the additional SiO_2 must necessarily come out of the frit.

Along with this series the glaze before mentioned as being reported by Dr. Mellor as the best type of leadless glaze thus far developed was made up as given in the Transactions, English Ceramic Society, vol. 12, page 7, using Cornwall stone in place of feldspar in its composition. The formula is as follows:

$$\left.\begin{matrix}.45\ K_2O(Na_2O)\\ .54\ CaO\\ .01\ MgO\end{matrix}\right\}.55\ Al_2O_3\left\{\begin{matrix}3.5\ SiO_2\\ 1.20\ B_2O_3\end{matrix}\right.$$

The mixtures of the various glazes, expressed in parts by weight, are compiled in the following table, No. 1:

TABLE 1

FRIT MIXTURES

Glaze numbers	B1	B2	B3	C1	C2	D1	D2	D3	E1	E2	E3	D1a	D1b	D1c	D1d
Feldspar	104.44	104.44	104.44	139.25	139.25	208.88	208.88	208.88	208.88	208.88	208.88	246.75	246.75	246.75	164.50
Borax	23.88	23.88	23.88	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	47.75
Whiting	50.00	50.00	50.00	50.00	50.00	37.50	37.50	37.50	37.50	37.50	37.50	25.00	25.00	25.00	25.00
Barium carbonate	24.63	24.63	24.63	24.63	24.63	24.63	24.63	24.63	24.63	24.63	24.63	24.63	24.63	24.63	49.26
Magnesium carbonate	5.25	5.25	5.25	5.25	5.25	5.25	5.25	5.25	5.25	5.25	5.25	10.50	.....	10.50	10.50
Strontium carbonate	9.19	9.19	9.19	9.19	9.19	9.19	9.19	9.19	9.19	9.19	9.19	18.38	18.38	.....	.....
Boric acid	3.91	38.75	62.00	54.25	77.50	77.50	155.00	155.00	77.50	155.00	155.00	77.50	77.50	77.50	46.50
Flint	84.60	105.00	105.00	93.75	127.50	105.00	105.00	67.50	90.00	90.00	52.50	51.00	51.00	51.00	94.50
Clay	.....	.....	.....	.....	.....	.....	.....	.....	32.25	32.25	32.25	.....	.....	.....	32.25
Zinc oxide	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	10.13	10.13	.....

GLAZE MIXTURES

Frit	208.00	240.00	250.35	255.55	293.00	325.00	360.00	330.00	335.28	370.24	340.24	315.84	319.92	313.60	317.60
Feldspar	55.70	55.70	55.70	55.70	55.70	55.70	55.70	55.70	55.70	55.70	55.70	65.80	65.80	65.80	65.80
Whiting	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00
Clay	25.80	25.80	25.80	25.80	25.80	25.80	25.80	25.80	25.80	25.80	25.80	25.80	25.80	25.80	25.80
Flint	16.32	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....

3. MATERIALS USED

The materials used in these glazes were Ohio silica flint; potash feldspar from the Maine Feldspar Co., Auburn, Me.; M. G. R. No. 2 English china clay and Great Beam English ball clay from Moore and Munger, New York; Cornwall stone from the Mayer China Co., Beaver Falls, Pa., together with the other standard glaze materials.

The ultimate chemical analyses of some of these materials are as follows:

TABLE 2

Ultimate Analyses of Some of the Materials Used.

	Ohio silica flint	Maine feldspar	M. G. R. No. 2 English china clay	Great beam English ball clay	Whiting	Cornwall stone
	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent
SiO_2	99.23	70.79	46.63	46.55	0.74	72.21
Al_2O_3	.32	16.75	37.13	38.38	.46	16.32
Fe_2O_3	.10	.22	.62	.93	.15	.00
TiO_2	.00	.00	.81	.05	.00	.00
CaO	.08	.24	.72	.25	55.16	2.02
MgO	.13	.18	.19	.23	.20	.20
K_2O	.00	8.26	.33	.70	.00	4.39
Na_2O	.00	3.29	.12	.25	.00	2.86
Loss on ignition	.22	.46	13.35	12.80	43.38	1.97
Total	100.08	100.19	99.89	100.14	100.09	99.97

The formula of the feldspar is:

$$\left.\begin{matrix}.60\ K_2O \\ .35\ Na_2O \\ .03\ CaO \\ .03\ MgO\end{matrix}\right\} 1.08\ Al_2O_3 \left\{\begin{matrix}7.76\ SiO_2 \\ .01\ Fe_2O_3\end{matrix}\right.$$

Comb. weight 658.4.

The formula of the Cornwall stone:

$$\left.\begin{matrix}.3490\ K_2O \\ .3445\ Na_2O \\ .2691\ CaO \\ .0374\ MgO\end{matrix}\right\} 1.1958\ Al_2O_3 \left\{\begin{matrix}8.995\ SiO_2 \\ .8221\ H_2O\end{matrix}\right.$$

Comb. weight 745.2.

4. UNDERGLAZE COLORS USED

The six standard underglaze colors used in the work have the following compositions:

Pink:	Per cent
Tin oxide	50.0
Whiting	25.0
Flint	18.0
Potassium bichromate	3.0
Borax	4.0
	100.0

Yellow:	
Alumina	8.0
Tin oxide	16.0
Black oxide of antimony	32.0
Red lead	44.0
	100.0

Brown:	
Ferric oxide	18.0
Chromium oxide	17.0
Alumina	11.5
Zinc oxide	53.5
	100.0

Victoria green:	Per cent
Chromium oxide	50.0
Flux	50.0
	100.0

Flux:	
Flint	30.0
Potassium bichromate	6.0
White lead	3.0
Whiting	3.0
Potassium nitrate	1.0

Blue green:	
Chromium oxide	20.0
Cobalt oxide	5.0
China clay	27.5
Spar	27.5
Zinc oxide	20.0
	100.0

Blue:	
Cobalt oxide	44.5
Alumina	55.5
	100.0

5. METHOD OF PREPARING THE GLAZES

All frits were weighed out, thoroughly mixed in the dry state, and fritted in a small crucible drop frit furnace, the frit being caught and chilled in water. Wherever clay was called for in any of the frits, English china clay was used. After the frits were prepared, dried and pulverized fine enough for the ball mill, the whole glaze batch was weighed out, sufficient water added, and the glaze ground in a porcelain ball mill until it would pass a 200-mesh lawn. In the glazes of series No. I English ball clay was used for the raw clay of the glaze batch, and in series No. II English china clay was used for the purpose of comparing the effect of the two clays on the settling and on the dipping behavior of the glazes.

After lawning, the glazes were placed in glass jars, allowed to settle, and all excess water was siphoned off. A few drops of a saturated solution of magnesium sulphate were used in all cases to bring the glazes to just the right dipping weight or thickness.

6. PREPARATION OF THE TRIALS

The trial pieces were small butter dishes of a hard nonabsorbent porcelain body supplied through the kindness of Mr. Ernest Mayer, of the Mayer China Co. The six underglaze colors were applied upon these dishes in narrow bands as used in decorating. The trials were then appropriately marked and dipped half in the leadless trial glaze and half in a standard lead glaze.

The lead glaze used was a very brilliant one and one that has been used commercially with perfect satisfaction. Its formula is as follows:

Glaze

$$\left.\begin{matrix}.0640\ K_2O\\ .1920\ Na_2O\\ .4903\ CaO\\ .2534\ PbO\end{matrix}\right\}.2811\ Al_2O_3\left\{\begin{matrix}2.8070\ SiO_2\\ .3845\ B_2O_3\end{matrix}\right.$$

Frit

$$\left.\begin{matrix}.0311\ K_2O\\ .2727\ Na_2O\\ .6962\ CaO\end{matrix}\right\}.2713\ Al_2O_3\left\{\begin{matrix}2.5471\ SiO_2\\ .5459\ B_2O_3\end{matrix}\right.$$

.704 equiv. of frit used.
Comb. wt. 277.52.

The glaze and frit mixtures in parts by weight are as follows:

Frit mixture:		Glaze mixture:	
Feldspar	17.3	Frit	195.37
Borax	104.2	Feldspar	23.39
Whiting	69.6	White lead	65.38
Clay	61.9	Clay	12.38
Flint	112.8	Flint	39.91
	365.8		336.43

7. FIRING THE TRIALS

The glazes of series No. I were fired at both Seger cones 1 and 3. Those of series No. II were carried to cone 3 only. The trials were fired in saggers washed with a very thin coat of the standard lead glaze, in a large test kiln, with natural gas as fuel. The duration of each burn was approximately 24 hours. The kiln was cooled rapidly in all cases.

III. RESULTS

In the following paragraphs the appearance and condition of the glazes themselves and their effect on the underglaze colors at cone 1 (1070° C) and at cone 3 (1100° C) are reported.

Series No. 1

.35 Al_2O_3 GROUP

Glaze B1 at cone 1.—Glaze smooth but slightly immature. No opalescence noted. All colors good.

Glaze B1 at cone 3.—Glaze bright and smooth, but surface slightly wavy and eggshell-like in appearance. Possibly not quite mature. No opalescence noted. All colors good.

Glaze B2 at cone 1.—Glaze slightly immature. Quite strong opalescence. All colors good.

Glaze B2 at cone 3.—Glaze mature, bright, and smooth. A very slight eggshell surface. No opalescence. All colors good.

Glaze B3 at cone 1.—Glaze immature. Quite strong opalescence. All colors good.

Glaze B3 at cone 3.—Glaze bright and smooth, apparently mature, but slightly eggshell-like. Opalescence quite marked where glaze is thick and noticeable throughout the glaze, giving it a dull, milky appearance.

All glazes of the .35 Al_2O_3 group are immature at cone 1 and mature or nearly so at cone 3. Glaze B2 at cone 3 is the best glaze of the group. It is a very good glaze, being nearly equal in appearance to glaze D1, which proved to be the best developed in the whole series. It is slightly less brilliant and, being slightly eggshelled, has not so fine a surface texture. A little higher heat or a longer firing would probably overcome the slight eggshell appearance.

This group illustrates the increase of opalescence with increase of B_2O_3, the rest of the formula being constant.

.40 Al_2O_3 GROUP

Glaze C1 at cone 1.—Not tested.

Glaze C1 at cone 3.—A fine, bright, smooth glaze, fully matured. No opalescence. A better glaze than C2 at cone 3, and very nearly equal to glaze D1 at cone 3. All colors good.

Glaze C2 at cone 1.—Glaze slightly immature. Quite strongly opalescent. All colors good.

Glaze C2 at cone 3.—Glaze fine, bright, smooth, and mature. Shows slight opalescence where glaze is thick. This glaze is equal

to B2 at cone 3, except for the slight opalescence which it shows. The surface texture is good, but not quite equal to glaze D1 at cone 3.

.50 Al_2O_3 GROUP

Glaze D1 at cone 1.—Glaze very slightly immature, best gloss and transparency not quite developed. No trace of opalescence. All colors good.

Glaze D1 at cone 3.—The best glaze developed in the series. Mature, fine, bright, and smooth. Though not quite so brilliant as the standard lead glaze it is whiter in color. No trace of opalescence. All colors fine.

Glaze D2 at cone 1.—Glaze immature. Strong, milky opalescence. Pink destroyed. Other colors good.

Glaze D2 at cone 3.—Glaze still has the appearance of immaturity. Strong, milky opalescence. Pink color destroyed. Other colors good.

Glaze D3 at cone 1.—Glaze slightly immature and slightly opalescent. Bubbled especially where thick. Pink color destroyed, but others good.

Glaze D3 at cone 3.—Glaze mature and bright. A very slight tendency toward opalescence, but a strong inclination to bubble, especially where the glaze is a little thick. Pink color is destroyed. Other colors good.

All of the glazes of the .50 Al_2O_3 group are slightly immature and opalescent at cone 1 except D1, which shows no opalescence. Glaze D1 at cone 3 is the best glaze developed in the series. The higher alkali and lower lime content, as well as the rather high B_2O_3, all help to make this glaze brilliant. The underglaze colors are all excellent. It has a brilliancy, transparency, and surface texture nearly, if not quite equal, to the standard lead glaze and a whiteness that is superior.

The glazes of this, as well as those of the .60 Al_2O_3 group, show that all compositions containing 1.0 B_2O_3 will spoil the chrome-tin pink color. Glazes D2 and D3, also E2 and E3, show that with the formula otherwise the same and where the B_2O_3 is already high an increase in the SiO_2 increases the opalescence, as Seger has pointed out.

.60 Al_2O_3 GROUP

Glaze E1 at cone 1.—Glaze slightly immature and milky from immaturity. No opalescence. All colors good.

Glaze E1 at cone 3.—Glaze bright and smooth, but appears to be still slightly immature. No opalescence. All colors good. It gives promise of being equal to glaze D1 at a little higher temperature.

Glaze E2 at cone 1.—The glaze appears to be mature, but the surface is eggshelled. Strong tendency to bubble where glaze is thick. Practically no opalescence. Pink destroyed, but other colors good.

Glaze E2 at cone 3.—Glaze mature, but surface eggshelled. Strong tendency to bubble. Practically no opalescence.

Glaze E3 at cone 1.—Glaze appears to be mature, but bubbles badly and destroys the pink color. No opalescence.

Glaze E3 at cone 3.—Glaze mature, bubbles badly where at all thick and destroys pink color. No opalescence.

The glazes of the .60 Al_2O_3 group containing 1.0 B_2O_3 show less opalescence than those of the .50 Al_2O_3 group, due to their higher Al_2O_3 content, but as a whole are not as good glazes at the temperatures used. The .60 Al_2O_3 content seems to have raised their maturing temperature somewhat.

Series No. II

This series, designed to improve glaze D1 if possible by varying the RO fluxes, failed to give any glaze quite equal to D1 in all respects.

Glaze D1a at cone 3.—A fine, bright, mature glaze, about equal in surface texture and brilliancy to D1. Shows no opalescence. It, however, destroys the pink color, probably due to too low a lime content in the glaze.[6] All other colors good.

Glaze D1b at cone 3.—A bright, smooth glaze, but with quite a marked tendency to develop many minute bubbles. It destroys the pink color and alters the shade of the greens. The change in the greens from green to an olive or brown is due to the ZnO in the glaze.

[6] Trans. Am. Cer. Soc. *14*, pp. 176–7.

Glaze D1c at cone 3.—A bright, smooth glaze with the same faults as glaze D1b.

Glaze D1d at cone 3.—A fine, bright, smooth glaze, but with a tendency to bubble where thick. It destroys the pink colors, probably for the same reason as given under D1a above.

The Mellor glaze at cone 3.—A bright, smooth glaze, but has a very bad effect on colors. It destroys the pink and yellow, flows the blue, and in general has a strong tendency at this heat, at least, to flow or drain on sloping surfaces and to bubble where at all thick.

IV. DISCUSSION OF RESULTS

The results of this investigation confirm Seger's findings in regard to leadless glazes in every particular. In the first place we observe that in general an increase in B_2O_3 in a given glaze increases opalescence. This point is brought out very nicely in the .35 Al_2O_3 group of series No. .I We also note that in order to avoid opalescence in this type of glaze, we must have a high content of alumina, and at the same time a comparatively low content of SiO_2. In a glaze high in B_2O_3 any increase in SiO_2 over that necessary for a stable and bright glaze will aid the B_2O_3 in increasing opalescence.

In glazes with .5 B_2O_3 or less it is quite noticeable that we get opalescence as soon as the molecular coefficient of the B_2O_3 in the formula becomes greater than that of the Al_2O_3, the SiO_2 remaining the same. In glazes with 1.0 B_2O_3 opalescence can be avoided with .5 Al_2O_3 to .6 Al_2O_3 if the SiO_2 is kept as low as possible.

In many of the trials it is also noticed that in a glaze which shows opalescence slightly this defect is often entirely removed by a longer or a somewhat higher heat treatment. This has been noted by others.[7]

Let us now see in what measure the leadless glazes developed in this work are able to fulfill the requirements set forth earlier.

1. *Dipping.*—Both English ball clay and English china clay were used as the raw clay added in the glaze batch and both were found to work well. None of the glazes settled. Those made up with ball clay seemed to dip a little better than the others in that

[7] Trans. Eng. Cer. Soc., Vol. 10, p. 129.

they appeared to adhere somewhat better and more evenly to the ware. There is the danger, however, of getting a bad color from the use of ball clay. Florida kaolin would obviate this difficulty and at the same time give sufficient plasticity. No difficulty in dipping has been reported by other investigators so far as known, and the writer believes that a leadless glaze can be made to dip equally as well as a lead glaze if prepared with care and intelligence.

2. In regard to heat range we can say that leadless glazes in general do not possess so long a range of fusion, but that the maturing limits, though a little higher in the temperature scale, are sufficiently wide to take care of the variations met with in very uniform firing. Leadless glazes do not flow as readily as those made with lead and therefore do not cover bare spots as well. Neither do they for the same reason flow colors.

There are many interesting opinions and facts on this subject in the report of the English "Lead Commission," published in London in 1910. In the investigation which the commission made of the use of lead in the potteries equally reliable firms testified that the number of "seconds" was and was not greater from the use of leadless glazes. The majority, however, state that the number of "seconds" is larger and that from this cause the cost of manufacture is at least 10 per cent greater.

3. *Underglaze colors.*—The best leadless glazes developed in this study have a beneficial rather than a detrimental effect on the colors tested. It is also possible that a number of colors not now in use under lead glazes can be developed for use under leadless glazes. As has already been stated, all glazes containing 1.0 B_2O_3 destroy the pink color; in fact this tendency is noticed in a very slight degree with glazes containing as low as 0.5 B_2O_3, though the pink still remains a strong and pleasing color. It is noted also that such glazes as D1 do not flow blues, for example, as much as lead glazes under such accidental conditions as too thick a dip, where the color has been used on a sloping or vertical surface. It must also be said, however, that if leadless glazes are dipped too thick they have a tendency to dull the colors.

4. *Appearance and durability.*—The consensus of opinion among English manufacturers who are using leadless glazes seems to be

that for the grades of ware for which they at present employ leadless glazes, they produce ware of an equally pleasing, though not identical, appearance, the leadless glaze being whiter and a little less brilliant.

Mr. Ernest Mayer, of the Mayer China Co., in the course of the work produced a few small pieces of ware of very creditable appearance compared with a standard lead glaze. The differences mentioned above were noted and seem to be inherent characteristics of this type of glaze. These glazes are harder by test than the lead glazes, and their durability has been pretty thoroughly established by actual use.

5. *Cost.*—The cost of the raw materials for leadless glazes is about equal to or a little less than that for lead glazes. The cost of the glazing operation is no more, but the loss from "seconds" is and probably will continue to be greater, especially in the better grades of ware. This is partially offset, however, by the saving in the expense necessary to provide the special safeguards for employees where lead glazes are used, or incurred in complying with the laws regulating the use of lead in potteries where such laws are in force.

V. CONCLUSIONS

The most authoritative report that we have at the present time on the subject of the practical use of leadless glazes is the above-mentioned report of the investigation in England by the "Lead Commission." This gives the actual experience and opinion of many English manufacturers who have been using or attempting to develop leadless glazes for many years past, due largely to the stringent English laws regulating the use of lead in the potteries. In the United States, as far as known, there are no leadless glazes used for white ware, china, or porcelain tableware.

As is to be expected during the period of its development, we find in this English report almost exactly opposite opinions expressed on almost every point discussed in regard to leadless glazes. From a technical standpoint this diversity of opinion is interesting, and shows that we are progressing, but that there is still much more to be learned regarding leadless glazes. We can afford to make mistakes in experimentation, as it is only by these mistakes

that we progress in our knowledge of the subject. However, when we come to consider the matter from a practical and commercial standpoint we must be more conservative, for here we can not afford to make mistakes. In the writer's opinion it would be very premature at the present time to say that we can make a leadless glaze for white-ware, china, or porcelain that could be substituted for the present lead glazes. Both have special faults and special virtues, but for use under general factory conditions, make them as perfect as we can, we are not likely to find any element, compound, or combination of compounds which will exactly duplicate the many excellent properties of lead as a glaze ingredient.

I desire to acknowledge my indebtedness to Prof. A. V. Bleininger, of the Bureau, and to Mr. Ernest Mayer, of the Mayer China Co., for many helpful suggestions and for assistance in making some of the tests during the course of this investigation.

WASHINGTON, December 15, 1913.

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